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CI. *The Efficiency of Production of Fluorescent X-Rays.*

By Arthur H. Compton, *Professor of Physics at the University of Chicago* *.

THERE exists a simple theory of the mechanism by which fluorescent X-rays are produced, which gives a definite prediction of the intensity of these rays. According to this theory, when an electron in the K energy level of an atom absorbs a quantum of X-rays, it is ejected as a photoelectron. An electron from the L or outer levels will then fall into the K level, resulting in the emission of a quantum of K series X-rays. For each quantum of energy absorbed by the K electrons there should thus be emitted one quantum of fluorescent X-rays of the K type. The ratio of the absorbed to the emitted rays can thus be directly calculated.

This simple theory has, however, predicted two important results which are inconsistent with experiment. The intensity of the fluorescent X-rays is found not to be as great as this theory indicates; and the β-rays excited by the X-rays are found to be more plentiful than it predicts. Both of these facts are indicated by the data accumulated by Sadler[*] and have been emphasized by Barkla[†] and by Barkla and Dallas[‡].

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* Communicated by the Author.

The Compound Photoelectric Effect and Fluorescent Yield.

A source of difficulty with the theory was made evident by Auger's discovery in 1925[§] of the "compound photoelectric effect," *i. e.*, the simultaneous ejection of several β-particles from the same atom. By measuring their ranges[||] he found that in addition to the photoelectron whose velocity is given by Einstein's equation

$$E_{kin} = h\nu - h\nu_K$$

for absorption by a *K* electron, there might be emitted from the same atom an electron of energy

$$E = h\nu_K - 2h\nu_L$$

and others of a similar type. The total energy of all the β-particles from a single atom was never more than $h\nu$. This observation showed that there are two different processes by which the atom can return to its normal condition. The first process is that in which the energy liberated when the atom returns to its normal state is radiated as a fluorescent ray. In the second process the energy absorbed by the atom is spent in ejecting from the atom one or more electrons. This may be considered either as a kind of internal photelectric absorption, or, as Auger thinks more reasonable, a radiationless energy transfer of the type which Klein and Rosseland describe as an "event of the second kind." Such an event—the transfer of the energy of an excited atom to an electron—has been recognized for some time in optics, and Rosseland had opined[¶] that it should also appear in the X-ray domain. It is clear that the occurrence of events of this second type will result in less intense fluorescent radiation, and more intense β radiation, which is precisely what is needed to satisfy the demands of Sadler's and Barkla's work.

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[*] C. A. Sadler, Phil. Mag. xvii. p. 739 (1909); xviii. p. 107 (1909); xix. p. 337 (1910).

[†] C. G. Barkla, Phil. Trans. ccxvii. p. 315 (1917).

[‡] C. G. Barkla and Miss Dallas, Phil. Mag. xlvii. p. 1 (1924).

[§] P. Auger, *C. R.* clxxx. p. 65 (1925); *J. de Phys. et Radium*, vi. p. 205 (1925).

[||] P. Auger, *Ann. de Physique*, vi. p. 183 (1926).

[¶] Rosseland, *Zeits. f. Phys.* xiv. p. 173 (1923). The suggestion that such an event might account for the anomalous ionization and fluorescence by X-rays was suggested by Kossel, *Zeits. f. Phys.* xix. p. 333 (1923), and by Barkla and Dallas, Phil. Mag. xlvii. p. 1 (1924).

Auger * has determined the probability that an event involving fluorescence will occur by the direct method of counting the number n of photoelectrons ejected from the K shell of an element (these can be identified for the heavier elements, because the range is shorter than that of a photoelectron ejected from an outer level), and comparing this with the number n_2 of atoms from which go associated tracks of the second kind. The difference $n-n_2$ is the number n_1 of fluorescent quanta emitted. He thus obtains what is known as the "fluorescence yield,"

$$w=n_1/n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

His results are summarized in the following table :

TABLE I.

Element.	Voltage.	w.
19 A	70 kv	·07
36 Kr	70	·5
	22	·51
54 Xe	43	·71

The experiments on krypton, using two different wave-lengths of primary X-rays, indicate that the fluorescence yield is a property of the atom and is independent of the wave-length of the exciting radiation. It is evident from these results that especially for the lighter elements the compound photoelectric effect is of relatively great importance.

Fluoresence Yield from Measurements of Fluorescence.

It is also possible to determine the fluorescence yield from measurements of the intensity of the fluorescent rays. If the compound photoelectric effect is the sole cause of the difficulty with the simple theory outlined above, the yield thus calculated should be identical with that determined by Auger. Kossel* and Bothe† have calculated approximate values of this factor using the fluorescence data given by Sadler and Barkla respectively. Kossel's results are :—

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* P. Auger, *Ann. de Physique,* vi. p. 183 (1926).

TABLE II.

	24	26	27	29	30
Element	Cr	Fe	Co	Cu	Zn
w	·23	·32	·39	·42	·51

These values are of the same order of magnitude as those of Auger, but vary with atomic number at a surprising rate. Kossel himself evidently does not have much confidence in their reliability, since he remains uncertain whether the experiments really show that w is less than 1. His work is of especial interest, however, in that he was led from these figures to give the first suggestion of atomic transformations of the second kind in order to account for a fluorescence yield less than unity.

The values of w calculated by Bothe, 0·5 for Br and 0·23 for Cr, fit more acceptably than do Kossel's with Auger's data. Jauncey and De Foe‡ have also made a rough measurement of the ratio of the fluorescent energy from copper to the absorbed rays, leading to a value of the fluorescence yield less than unity.

Since Auger's discovery of the compound photoelectric effect, two measurements of the fluorescence yield have been made, one by Balderston § and one by Harms ‖. Balderston compares the total number of absorbed quanta with the number of fluorescent K quanta, calling the ratio u. Since only about $\frac{7}{8}$ of all the absorbed quanta are absorbed by the K shell, his ratio u must be divided by $\frac{7}{8}$ in order to get the fluorescence yield, w, which is comparable with Auger's data. As thus corrected, his values are :—

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* W. Kossel, *Zeits. f. Phys.* xix. p. 333 (1923).

† W. Bothe, *Physik. Zeits.* xxvi. p. 410 (1925).

‡ G. E. M. Jauncey and O. K. De Foe, Proc. Nat. Acad. xi. p. 520 (1925).

§ L. Balderston, Phys. Rev. xxvii. p. 695 (1926).

‖ M. I. Harms, *Ann. d. Phys.* lxxxii. p. 87 (1926).

TABLE III.

	26	28	29	30	42	47
Element ...	Fe	Ni	Cu	Zn	Mo	Ag
w	·38	·45	·50	·57	·95	·86

The experimental error in these determinations is probably large. Balderston calls attention to an uncertainty of 13 per cent. in the solid angle subtended by the window of the ionization chamber. Errors which are probably of the same order of magnitude are introduced also by uncertainty in the absorption in the ethyl bromide vapour, and by the method of calculation, which involves an extrapolation, assuming a linear variation over a range of wave-lengths in some cases more than 3 times the range over which observations were taken. More serious errors of a consistent nature are apparently introduced by the assumption that the ionization of different wave-lengths in air is proportional to the absorption in air, whereas for the shorter wave-lengths a large part of the absorption is due to scattering, and does not result in ionization. Also, since in his experiments the fluorescent rays struck the side walls of the ionization chamber, whereas the primary rays did not, it was not possible to compare the relative intensities, even of the same wave-length, by comparing the ionizations. These values can therefore be assigned but little weight.

Harms* has made a more careful analysis of the problem. In the following table his results are given in columns 2 and 3.

TABLE IV.

Element.		w'.	w.	w (corrected).
26	Fe	·530	·303	·282
29	Cu	·589	·394	·378
30	Zn	·598	·418	·403
34	Se	·647	·530	·517
38	Sr	·598	·590	·615
42	Mo	·754	·754	(·730)

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* M. I. Harms, *loc. cit.*

In calculating w' Harms has made use of Kossel's relation between the wave-length and the ionization current per erg of β-ray energy. As he himself notes, Kulenkampff * and Kircher and Schmitz † have independently reached the conclusion that from ·5A to 1·5A there is a strict proportionality between absorbed energy and ionization. Yet Kossel considers the older work of Lenard and Holthusen more reliable, and Harms has used Kossel's correction factor to calculate the energy from the ionization. The conclusion of Kulenkampff and of Kircher and Schmitz has recently been confirmed by Crowther and Bond ‡, and is supported by the results about to be described. Harms's data should thus not have been corrected by Kossel's factor, and he should have obtained the values of w given in column 4.

There are some minor corrections that should be applied to Harms's results :—(1) The mass scattering coefficient of air for λ ·71 should be, from Hewlett's data on carbon §, not less than 0·20, whereas Harms has used the value 0·17 ; (2) a part of the secondary X-rays is scattered, whereas Harms assumes that it is wholly fluorescent. From my measurements this fraction varies from 4 per cent. in the case of λ ·71 A exciting secondary rays in iron to 0·4 per cent. in selenium ; (3) the value for strontium was obtained using a surface of strontium sulphate instead of the element, and a correction of 5 per cent. must be applied to make it comparable with the values for the other elements ; (4) the value for molybdenum is an extrapolated one, assuming that the variation of w with the atomic number is linear. This assumption probably is not justified. These minor corrections give us the values in the last column.

Harms's measurements are subject to some uncertainty, because the intensity of the primary and fluorescent beams were measured by two ionization chambers of very different design. The measurements thus involved a comparison of the capacities of the two systems, the sensitivity of the two electrometers, and the effective path of the X-rays in the two ionization chambers. Moreover, he used a beam from a molybdenum target, filtered through

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* H. Kulenkampff, *Ann. der Phys.* lxxix. p. 97 (1926).

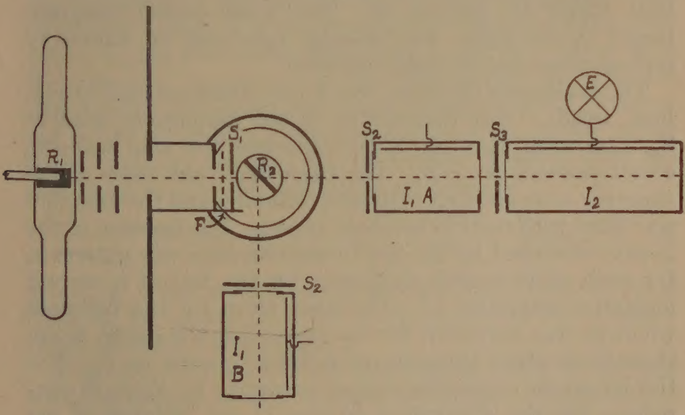
† H. Kircher and W. Schmitz, *Zeits. f. Phys.* xxxvi. p. 484 (1926).

‡ J. C. Crowther and W. N. Bond, Phil. Mag. vi. p. 401 (1928).

§ C. W. Hewlett, Phys. Rev. xvii. p. 284 (1921).

a zirconium screen, and assumed that the effective wavelength of the transmitted rays was that of the K lines. A spectral analysis of the X-rays under these conditions * shows that ordinarily only about 25 per cent. of the filtered beam consists of the Kα lines, and that there is a band of the continuous spectrum in the neighbourhood of 0·5A which has more energy than has the Kα radiation. This heterogeneity makes it impossible to estimate the absorption accurately from tables of absorption coefficients, as Harms found it necessary to do. It would, nevertheless, seem that Harms's values of the fluorescence yield, after applying the corrections noted above, are more reliable than those of the other investigators.

Fig. 1.



New Measurements of the Fluorescent Yield.

In view of the unsatisfactory status of these fluorescence measurements, I have undertaken some new measurements of the fluorescence yield. These measurements were meant to be of only a preliminary character ; but as they have led to results that seem more reliable than those now in the literature, and since it is uncertain when the experiments can be continued, it seems worth while to publish them at this time.

The apparatus used in my experiments is shown in fig. 1, which is drawn approximately to scale.

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* A. W. Hull, Phys. Rev. x. p. 666 (1917).

Nearly homogeneous X-rays were obtained by taking the fluorescent rays from plates of various elements placed at R_1, just over the X-ray tube*. These homogeneous rays were limited by a diaphragm S_1, and fell on the radiator R_2 whose fluorescence yield was to be determined. R_2 was a flat thick plate placed at 45 degrees on the crystal table of a Bragg spectrometer, and of area large enough to intercept all the rays coming through the diaphragm S_1. The fluorescent rays from R_2 entered the ionization chamber I_1 at its position B, through a lead diaphragm S_2. The ionization current thus obtained was compared with that observed when the chamber was turned to the position A, with the radiator R_2 removed, and with a second diaphragm at S_1 of opening small enough so that the ionization current was of the same order of magnitude as that found in position B. The water-cooled tungsten target X-ray tube was usually operated at about 40 milliamperes and 53 peak kilovolts.

The ionization chamber was 8 cm. diameter and 11 cm. long, inside. The dimensions of the diaphragm used at S_2 were such that no X-rays reached the side walls in either position A or B. The front and back faces of the chamber were covered with thin celluloid, and the chamber was filled with methyl bromide vapour. The fraction of the X-rays absorbed by the gas in the chamber was measured for each wave-length employed by the use of a second ionization chamber I_2. The absorption by the celluloid windows was corrected for by measuring the direct beam through an equal thickness of celluloid placed at F. For the longer-wave-lengths it was necessary to apply a correction for the absorption in the 11 cm. column of air displaced by the ionization chamber.

Calculation of the Fluorescence Yield.

The intensity of the fluorescent X-rays may be calculated as follows: If μ' is the total absorption coefficient of the primary X-rays in the radiator, we have

$$\mu' = \sigma' + \tau', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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* The high degree of homogeneity thus obtained was recognized long ago by Barkla, and has recently been investigated by the writer (Proc. Nat. Acad. xiv. p. 549, 1928). In the latter paper I failed to mention the work of Allison and Duane (Proc. Nat. Acad. xi. p. 486, 1925), who also call attention to this remarkable homogeneity.

where τ' is the photoelectric absorption, and σ' is the absorption due to scattering. If, as is the case in these experiments, the primary wave-length λ' is shorter than the critical K absorption wave-length of the radiator λ_K, the greater part of the photoelectric absorption is that due to the electrons in the K shell, τ_K'. Let us suppose that a beam of intensity I′ and of cross-section A′ traverses a thickness *ds* of the radiator. The number of quanta absorbed by the K electrons, and hence the number of photoelectrons ejected from the K energy levels of the atoms will then be

$$dn = \mathrm{I}'\mathrm{A}'\tau_K' ds \,.\, \frac{1}{h\nu'}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ν' is the effective frequency of the primary rays. By equation (1), the number of fluorescent quanta is then $dn_1 = w\,dn$, where w is the fluorescence yield, and the total power in the fluorescent beam will be $h\nu'' dn_1$, where ν'' is the effective frequency of the fluorescent ray. Barkla and Sadler have shown that the intensity of the fluorescent ray is the same in all directions. Thus the power in the fluorescent ray entering the ionization chamber from the thin layer *ds* (uncorrected for absorption) is

$$d\mathrm{P}'' = h\nu'' dn_1 \frac{\mathrm{A}''}{4\pi r^2} = \frac{w}{4\pi}\mathrm{P}'\frac{\mathrm{A}''}{r^2}\tau_K'\frac{\nu''}{\nu'}ds, \quad . \quad . \quad (4)$$

where A″ is the area of the diaphragm S_2, τ is the distance from R_2 to S_2, and $\mathrm{P}' = \mathrm{A}'\mathrm{I}'$ is the power in the primary beam striking the radiator.

If the fluorescent ray leaves the surface at the same angle with the normal as that at which the primary beam enters, the paths of the primary beam and of the secondary beam in the radiator are equal, having the value, let us say, s. Writing μ' and μ'' for the absorption coefficients of the two beams *, we thus have for the power in the fluorescent beam from a thick radiator,

$$\left.\begin{aligned}\mathrm{P}'' &= \frac{w}{4\pi}\mathrm{P}'\frac{\mathrm{A}''}{r^2}\tau_K'\frac{\nu''}{\nu'}\int_0^\infty e^{-(\mu'+\mu'')s}ds \\ &= \frac{w}{4\pi}\mathrm{P}'\frac{\mathrm{A}''}{r^2}\frac{\tau_K'}{\mu'+\mu''}\frac{\nu''}{\nu'}\end{aligned}\right\} \quad . \quad . \quad . \quad (5)$$

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* Strictly speaking, one should use an absorption coefficient intermediate between μ' and τ', since part of the primary rays scattered in the radiator are reabsorbed before leaving the radiator. However, μ' and τ' are so nearly equal that this difference can be neglected.

Writing instead of ν''/ν' its equivalent λ'/λ'', we obtain for the value of the fluorescence yield,

$$w=4\pi\frac{r^2}{\mathrm{A}''}\frac{\mu'+\mu''}{\tau_{\mathrm{K}}'}\frac{\lambda''\,\mathrm{P}''}{\lambda'\,\mathrm{P}'}. \quad . \quad . \quad . \quad . \quad (6)$$

The quantities r and A$''$ can be measured directly, λ' and λ'' are the weighted mean wave-lengths of the fluorescent radiations from the radiators R_1 and R_2 respectively *, and μ' and μ'' are the absorption coefficients in the radiator of the wave-lengths λ' and λ''. The values of μ' and μ'' have been interpolated from the tables of absorption data compiled by the writer †. According to Richtmyer and Warburton ‡, the coefficient k in Owen's formula for the photoelectric absorption per atom,

$$\tau_a=\mathrm{K}Z^4\lambda^3,$$

is 0·0224 on the short wave-length side of the K absorption limit and 0·0033 on the long wave-length side. The fraction $(224-33)/224=0\cdot85$ of τ is thus due to the K electrons. For absorption in the radiators here considered, the scattering term σ is less than 1 per cent. of μ and may be neglected in the calculation. We thus have,

$$\tau_{\mathrm{K}}'=0\cdot85\mu'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In order to obtain the ratio P''/P' from the experimental data, let us assume in accord with the results of Kulenkampff §, Kircher and Schmitz ||, and Crowther ¶ that the ionization is proportional to the energy spent in producing β-rays. Of the total energy absorbed in the methyl bromide vapour, the fraction τ/μ is spent in exciting photoelectrons (the part spent in exciting recoil electrons may be neglected). As we have seen, if the frequency is greater than the K limit of bromine, 85 per cent. of this is absorbed in the K shell, and 15 per cent. in the outer shells. If n_a is the total number of absorbed quanta, a number

$$n_f=0\cdot85w_{\mathrm{B}}\frac{\tau}{\mu}n_a$$

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* On the basis of the results of Unnewehr (Phys. Rev. xxii. p. 529, 1923) and the writer (Proc. Nat. Acad. xiv. p. 549, 1928) the ratio of the α lines to the β lines has been taken as 5 : 1 for the elements used.

† A. H. Compton, 'X-Rays and Electrons' (Van Nostrand, 1926), p. 184.

‡ F. K. Richtmyer and F. W. Warburton, Phys. Rev. xxii. p. 539 (1923).

§ H. Kulenkampff, *Ann. der Phys.* lxxix. p. 97 (1926).

|| H. Kircher and W. Schmitz, *Zeits. f. Phys.* xxxvi. p. 484 (1926).

¶ J. C. Crowther and W. N. Bond, Phil. Mag. vi. p. 401 (1928).

reappears as fluorescent K rays of frequency ν_{Br}''. The energy of the K rays escaping to the walls is thus

$$0\cdot85 w_{Br}\frac{\tau}{\mu} n_a h\nu_{Br}'' e^{-\mu''\bar{x}}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where μ'' is the absorption of the bromine K rays in the methyl bromide vapour, and x is the effective distance traversed by the rays before reaching the walls. An approximate calculation of $e^{-\mu''\bar{x}}$ gives 0·937. Noting that the absorbed energy is $n_a h\nu$, and that $\nu''/\nu=\lambda/\lambda''$, this means that the fraction of the absorbed energy lost as K radiation is

$$0\cdot85\times0\cdot937 w_{Br}\frac{\tau_{Br}}{\mu_{Br}}\frac{\lambda}{\lambda_{Br}''}=0\cdot796\left(w\frac{\tau}{\mu}\frac{\lambda}{\lambda''}\right)_{Br}.$$

Any fluorescent L or M radiation will be absorbed before reaching the walls of the ionization chamber, and hence will appear as β-ray energy. There are, however, also scattered rays from the methyl bromide vapour which escape from the ionization chamber without producing ionization. The number of such scattered quanta is $n=n_a\sigma/\mu$, of which a fraction $e^{-\mu'x}$ will escape from the chamber. Thus the total fraction of the absorbed energy which escapes from the ionization chamber is

$$0\cdot796\left(w\frac{\tau}{\mu}\frac{\lambda}{\lambda''}\right)_{Br}+e^{-\mu'x}\frac{\sigma}{\mu}.$$

If we call R the ratio of the energy spent in producing ionization to the absorbed energy, we thus have, for rays shorter than the K limit of bromine,

$$R=1-0\cdot796\left(w\frac{\tau}{\mu}\frac{\lambda}{\lambda''}\right)_{Br}-e^{-\mu'x}\frac{\sigma}{\mu}. \quad . \quad . \quad (9)$$

When λ is greater than $\lambda_{K\,Br}$ the second term in this expression becomes negligibly small.

Let i' and i'' be the ionization currents due to the primary and secondary rays respectively, f' and f'' the fractions of the two beams absorbed by the methyl bromide, and S′ and S″ be the areas of the slits S_1 used in the two cases. Then,

$$\frac{i''}{i'}=\frac{P''f''S''}{P f S'}\frac{R''}{R'}\frac{e^{-(\mu_a''r+x'')}}{e^{-(\mu_a'r+x')}}.$$

Here $\mu a'$ and $\mu a''$ are the absorption coefficients in air o the two beams, r is as before the distance from R_2 to the ionization chamber, and x' and x'' account for the absorption in the celluloid window. We thus have,

$$\frac{P''}{P'} = \frac{i'' f S' R'}{i' f'' S'' R''} \frac{e^{y''}}{e^{y'}}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $$y = \mu_a r + x.$$

Making use of equations (7) and (10), expression (6) now becomes

$$w = 14{\cdot}78 \frac{r^2}{A''} \frac{\mu' + \mu''}{\mu'} \frac{\lambda''}{\lambda} \frac{i''}{i'} \frac{S'}{S''} \frac{f'}{f''} \frac{R'}{R''} \frac{e^{y''}}{e^{y'}}. \quad . \quad (11)$$

The Measurement of Relative Intensities for different Wave-lengths.

It will be seen that an expression similar to equation (10) affords a means of comparing the power in two X-ray spectrum lines of different wave-lengths in terms of the ionization resulting from them. The appropriate form of the expression is

$$\frac{P_1}{P_2} = \frac{i_1 f_2 R_2}{i_2 f_1 R_1} \frac{e^{-y_2}}{e^{-y_1}}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where the significance of the various terms is as in equation (10). This expression, of course, does not correct for the difference in reflecting power of the grating for the two wave-lengths.

Evaluation of the Fluorescence Yield.

In the present experiment, referring to equation (11), $r = 15{\cdot}78$ cm., $A'' = 7{\cdot}70$ cm.^{2}, and the other quantities are given in the following table :

TABLE V.

Experiment.	λ'.	λ''.	$\frac{\mu'+\mu''}{\mu'}$.	$\frac{i''}{i'}$.	$\frac{S'}{S''}$.	$\frac{f'}{f''}$.	$e^{(y''-y')}$.	$\frac{R'}{R''}$.	w.
1. Sn → Mo	·482	·696	1·425	·370	·00374	·440	1·016	1·136	·69
2. Ag → Mo	·549	·696	1·290	·352	·00374	·588	1·013	1·093	·67
3. Sn → Se	·482	1·085	2·24	·727	·000472	·742	1·091	·788	·53
4. Mo → Se	·696	1·085	1·427	·866	·000472	1·69	1·073	·694	·55
5. Sr → Se	·859	1·085	1·334	·970	·000472	2·33	1·048	·622	·56
6. Sn → Ni	·482	1·629	4·69	·261	·000472	·343	1·316	·788	·33
7. Mo → Ni	·696	1·629	2·30	·441	·000472	·781	1·299	·694	·38
8. Sr → Ni	·859	1·629	1·75	·579	·000472	1·08	1·267	·622	·37
9. Se → Ni	1·085	1·629	1·40	1·39	·000472	·463	1·210	1·000	·37
10. Zn → Ni	1·410	1·629	1·292	1·42	·000472	·805	1·102	1·000	·42

The diaphragm apertures S′ and S″ can be measured directly. The ratios i''/i' are the ratios of ionization currents as read from the electrometer, except that corrections have been applied to take account of the scattered primary rays mixed with the fluorescent rays from R_1 and also for the scattered rays mixed with the fluorescent rays from R_2. These corrections were based on absorption measurements of the mixed rays. Only in the cases of tin rays falling on nickel and of the primary rays falling on zinc were these corrections large—that is, in cases 6 and 10. The absorbed fractions f' and f'' were measured directly by means of the auxiliary ionization chamber I_2. The absorption coefficients $\mu a'$ and $\mu a''$ used in calculating y' and y'' were interpolated from a table given by Siegbahn *.

In order to evaluate R′/R″, it was at first assumed that, since the atomic numbers of selenium and bromine are nearly the same, the fluorescence yield w will be the same for both. Expressing R in terms of w, as in equation (9), equation (11) can thus be solved for w in experiments 3, 4, and 5, giving the mean value $w = 0{\cdot}549$. In making this calculation, since under the conditions of these experiments σ was less than 1 per cent. of μ, the last term in equation (9) was neglected. Thus for wave-lengths greater than the K limit of bromine R may be taken to have the value 1. Using this value 0·549 for the fluorescent yield in bromine, provisional values of R for the other cases could be calculated, and provisional values of w determined for molybdenum and nickel. This showed the rate of change of w with atomic number, and indicated that if 0·542 is the mean value of w for bromine and selenium, its value for bromine should be ·565. Using this value for w_{Br}, and taking $\tau=\mu$, the values of R′/R″ shown in column 9 are calculated from equation (9). From equation (11) we then obtain the values of w given in the last column.

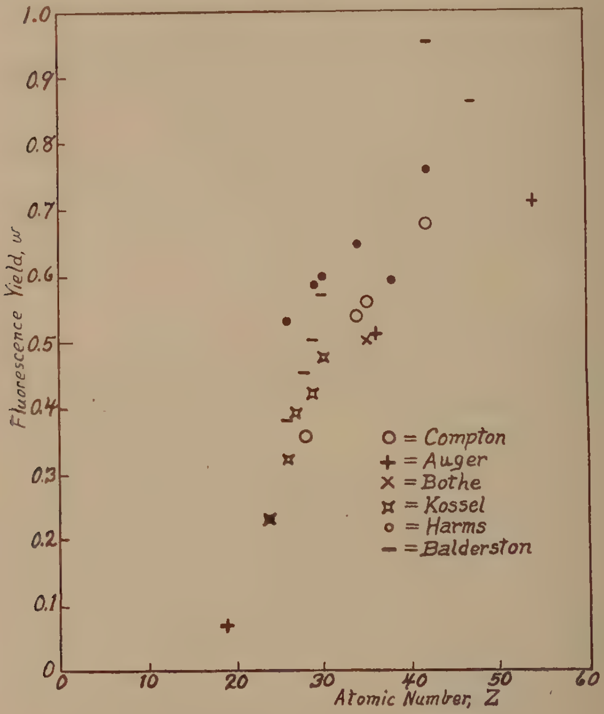
Discussion of Results.

There is no significant variation in the values of the fluorescence yield w with the wave-length of the exciting radiation. The only apparent departure from this statement is for the nickel radiator when excited by rays from

* M. Siegbahn, 'Spectroscopy of X-Rays,' p. 246.

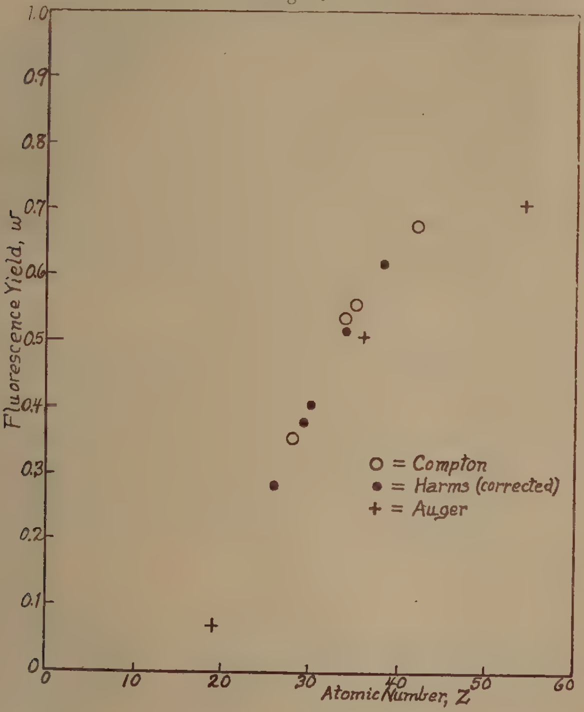
tin and from zinc. As we have noted, however, in these two cases the corrections due to the presence of scattered X-rays were so large as to make the results considerably less reliable than in the other cases. The experiments thus indicate (in support of the conclusions of all previous investigators) that the fluorescent yield is a constant characteristic of the radiator, but independent of the exciting radiation.

Fig. 2.



If we had assumed that the number of ions produced per unit energy by the β-rays in the ionization chamber were a function of the wave-length of the incident X-rays, as was assumed by Kossel and Harms, this independence of w of the exciting wave-length would not have appeared. For the efficiency of ion production by the fluorescent rays from any one radiator would have remained constant, while that due to the exciting rays would on this assumption have varied with their wave-length, resulting in a corresponding variation in w. In so far as the values of w here obtained are constant for a given radiator R_2 therefore, this work supports the conclusions reached by Kulenkampff, Kircher and Schmitz, and Crowther that the ionization by β-rays per unit energy is independent of their energy.

Fig. 3.



In fig. 2 are plotted the values of the fluorescence yield given by the different investigators. Of these, as we have seen, Auger's values have been obtained by the direct method of comparing the number of single photoelectrons with the number of compound photoelectrons. The results of Bothe, Kossel, and Balderston can be considered only as rough approximations, and Harms's values should be corrected for certain unjustified assumptions in the calculations. In fig. 3 Harms's values of w as thus corrected are compared with those of Auger and the writer. Their agreement with the writer's results is seen to be good.

If the assumption of Auger and Kossel is correct, that the compound photoelectric effect is the whole explanation of the fact that the fluorescence yield is less than unity, Auger's values should fall on the same curve with those of Harms and the writer. Though this agreement is not exact, it is probably within the limits of experimental error. The present work thus confirms Auger and Kossel's theory that the compound photelectric effect is responsible for the fact that the fluorescence yield is less than unity.

It will be noted that these experiments show a rapid increase of the fluorescence yield with increasing atomic number. For elements as light as aluminium, fluorescence should thus be almost non-existent. On the other hand, for a heavy element such as iodine, a larger portion of the absorbed energy is spent in producing fluorescence and a smaller portion in producing ionization. This gives a lighter element, such as argon, a certain advantage for use in an ionization chamber, though in this case it is, of course, more difficult to secure complete absorption.

Of practical significance is the fact that, having a knowledge of the fluorescence yield, it is now possible to make a reliable calculation of the relative intensity of X-ray beams of different wave-lengths, in terms of the ionization which they produce. The necessary formula is given in equation (10).

SUMMARY.

A review of the published data describing the intensity of fluorescent X-rays shows that the various observers agree that the number of quanta of fluorescent X-rays emitted by a radiator is considerably less than the number of quanta which it absorbs from the primary beam. The values of the efficiency of fluorescence that appear in the literature are for the most part, however, found not to be quantitatively reliable.

New experiments give values of the "fluorescence yield," or ratio of the number of fluorescent K quanta to the number of photoelectrons ejected from the K shell, of 0·68 for a molybdenum radiator, 0·56 for bromine, 0·54 for selenium, and 0·37 for nickel. The values seem to be independent of the wave-length of the exciting rays.

These measurements agree within experimental error with Auger's values of the fluorescent yield, based on his count of the frequency of occurrence of the compound photoelectric effect, and thus indicate that it is this effect which makes the fluorescent yield less than unity.

An expression is derived for calculating the relative intensity of two X-ray beams of different wave-length, in terms of the ionization currents obtained and other factors.

Ryerson Laboratory,
University of Chicago,
December 13, 1928.

CII. *Arc and Spark Radiation from Hydrogen in the Extreme Ultra-Violet.* By JOHN THOMSON, *M.A., B.Sc., Ph.D., Lecturer in Physics in the University of Reading* [*].

Introductory.

THE purpose of the present communication is to describe certain experiments which reveal the ultimate source of the ionizing radiations emitted by point discharges in hydrogen. The work is a continuation of that described in previous papers [†]. In the present paper a method is suggested whereby the manner of excitation of the extreme ultra-violet radiations emitted by the gas may be determined, and, as far as the writer is aware, this method is entirely new. It might possibly be applied with success to problems other than the one discussed. The results obtained by it indicate that, under the conditions of the present experiments, by far the greater part of the radiation responsible for the ionization of the gas is emitted by *neutral* molecules or atoms. A small part of the radiation is definitely attributable to *ionized* molecules or atoms, however, and this part is of greater relative importance when the pressure of the gas is large.

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[*] Communicated by Prof. E. Taylor Jones, D.Sc. The writer performed the greater part of this work while a Carnegie Research Fellow in the University of Glasgow.

[†] J. Thomson, Phil. Mag. v. p. 513; vi. p. 526 (1928); vii. p. 970 (1929).

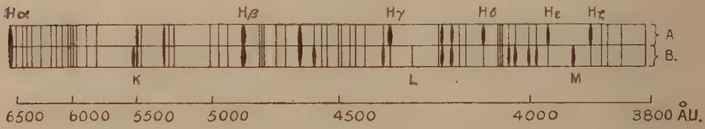
Theoretical considerations indicate that the new method for determining the source of the radiations has, in these experiments at least, given very plausible results, while the rough test of its basic hypothesis which has been performed is in every way satisfactory.

In the opening paragraphs of the communication some experiments are described concerning the possibility of ionizing radiations being emitted by the metal of the point electrodes themselves.

The Source of the Ionizing Radiations.

In one of the papers by the present writer already mentioned, "On the Ionization of Hydrogen by Its Own Radiations," it was tacitly assumed that the metallic points in a point discharge did not themselves emit ionizing radiations. The justification for this assumption depended upon an experiment performed in earlier work, where it was found that ionizing radiation was certainly emitted by *the gas in the vicinity of* the points, and also upon the evidence of other workers concerning the *visible* radiations from such a discharge. In all the experiments described in this and preceding papers the current flowing between the points (which were always of platinum) never exceeded 2 milliamp., and the only capacity in the circuit was the small self-capacity of the induction coil itself. But it has been shown by many spectroscopists that under such circumstances, and particularly where the electrodes are of platinum, the spectrum of the discharge is due almost entirely to the gas between the electrodes.

Fig. 1.



It was thought advisable, however, in view of the peculiar nature of the problem, to make some further investigation, and to this end spectrograms of the visible and near ultra-violet radiation from the discharge were taken. These were then compared with similar spectrograms of a hydrogen vacuum tube: copies of two typical spectra are shown diagrammatically in fig. 1.

Spectrum A was taken from the vacuum tube; B from the point discharge at atmospheric pressure with about 2 milliamp. flowing. It will be seen that the two spectra are very similar indeed. Out of the sixty or so clear lines present in both spectrograms only the three marked K, L, M in the spectrum of the point discharge are not definitely attributable to hydrogen, and of these three only one can possibly be due to platinum. This one line, M (3923 Å.U.), is the *raie ultime* of that element, and is visible when excited platinum is present as an impurity to the extent of one part in 10^{10}. Consequently, no great significance can be attached to its appearance in this case. In fact, the evidence of the spectrograms is all in favour of the view that the discharge radiations are due almost entirely to the gas.

In passing, an interesting feature of the spectrum of the point discharge may be noted. The spectrum of the vacuum tube consists essentially of the atomic spectrum—the Balmer series. The molecular spectrum in this case is decidedly "secondary." In the discharge at atmospheric pressure, however, the relative intensities of the two spectra are entirely changed. The molecular lines are more intense, while it is difficult to distinguish any of the atomic lines beyond H_γ.

To obtain, if possible, more direct evidence with regard to the source of the ionizing radiations, another experiment was performed.

A discharge-tube similar to that used in a previous investigation was fitted with two pairs of similar points, one pair being of platinum, the other of tin, and the distance between the first pair was made equal to the distance between the second pair. Then the intensity of the ionizing radiations from a discharge between the platinum points carrying 1 milliamp. was compared with the intensity of the radiations from a discharge between the tin points carrying 1 milliamp., the detector of the radiation being at the same distance from the source in both cases. The intensities were found to be equal within the limits of the experimental error, which was about 1 per cent. of the value of either intensity as indirectly measured by an electrometer. Now, if the source of any considerable part of the radiation was the metal of one of the electrodes, one would expect that the greater fusibility of the tin combined with the general dissimilarity of the metals would cause some distinct difference in the two intensities. That the result of the experiment was negative at least suggests that the radiations emanated from the gas.

The writer has so far been unable to find an *experimentum crucis* to decide conclusively between the two possible sources. All the evidence at present available strongly suggests, however, that the electrodes play no part in the radiation phenomena, and this hypothesis is eminently satisfactory in explaining the results of all the other experiments.

Measurements of the Intensities of the Radiations.

Previous investigations* had shown that there was much to be learned from a quantitative study of the variation in intensity of the radiations as the current flowing in the discharge was varied. The object of the new experiments was to exhaust the possibilites of such a mode of approach by utilising the refinements of technique suggested by previous work. The accuracy of the measurements involved was made the subject of careful investigation, so that accidental variations in readings might not be considered as real phenomena. It is claimed for the results which are to be given later that all the phenomena observed are characteristic of the gas hydrogen.

Experimental Arrangements.

The Gas System.—The experiments consisted essentially in measuring the ionization current in a region Q of a discharge-tube caused by the total radiation emitted by a point discharge in a region P. Maintaining the pressure of the gas at a constant value, this ionization current was measured for different values of the discharge current, the aim of the experiment being to determine the exact relation between the two currents. In a previous investigation it had been found that the value of the ionization current for a given discharge current at a given pressure depended to a very great extent on the purity of the hydrogen. It was therefore necessary to obtain the gas in as pure and dry a state as possible. To this end the hydrogen was generated electrolytically in a specially constructed Hoffmann's apparatus, designed to prevent the passage of oxygen from the anode to the cathode. To reach the discharge-tube the gas passed through a capillary tube, two tubes containing calcium chloride, a tube containing phosphorus pentoxide, and two liquid-air traps. One of the traps was in the discharge-tube system itself (*i. e.*, that part of the system sealed off when experiments were in progress), which also contained a simple pressure gauge, and was connected through a vacuum stop-cock to a Hyvac pump. The entire gas system was glass sealed, thus avoiding any foreign vapours from wax or rubber.

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* *Loc. cit.* vi. p. 526 (1928).

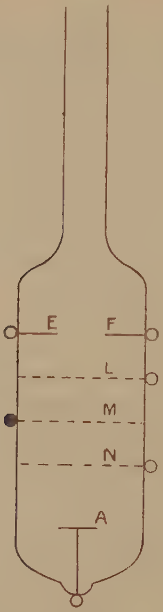
Such a system does not, of course, give pure gas when first used. The glass, the powdered phosphorus pentoxide and calcium chloride, and the glass wool which was also included, all contain much occluded gas and vapour: but, if the system is evacuated and filled with hydrogen a large number of times, sufficient time being allowed after each filling to dry the gas thoroughly over the drying agents, then the moisture disappears from the glass, and the occluded gases are displaced by the hydrogen. In the present experiments it was found to be unnecessary to use liquid air. When the gas was allowed to remain over the drying agents for four or five days, it was found to be fairly dry on entering the tube.

The tests of the purity and dryness of the gas were such as had been suggested by previous investigation. These tests depend upon two properties of the impure gas described in a former paper. If any oxygen is present in the discharge-tube, the ionization current caused by the discharge persists for some time after the latter has been cut off. The magnitude of this residual current is a rough measure of the amount of impurity present in the tube. This test is a very delicate one, as has been shown repeatedly in the course of this and previous experiments. An even finer test, however, is given by the variation of the ionization current when the pressure and discharge current are kept constant, the same sample of gas being used for a number of readings. When the dry gas is introduced into the tube, the ionization current has a comparatively large value. If, however, the tube itself is not dry, successive readings show a diminution in the ionization, indicating that the tube is giving up its moisture to the gas. This test still gave a positive result after the apparatus had been in use for a month. The diminution in the ionization is a consequence of the fact noted in a previous communication that the drier and purer the gas the greater is the ionization produced. When these tests failed to detect any impurity in the gas, it was assumed that the experiments could be performed with safety.

The Discharge-Tube :—This has already been described in a previous paper. It is shown diagrammatically in fig. 2.

The tube was cylindrical in form with one outlet tube K to connect it to the gas system. E and F were the points of two platinum electrodes one-half centimetre apart. L, M, N were three circular pieces of wire gauze, while A was a small copper plate coated with copper oxide (CuO). During the experiments L was maintained at a potential of —310 volts. M, which was 1 centimetre below L, was connected to earth, while N, 1 centimetre below M, was maintained at −310 volts. A was about 1½ cm. below N, was connected to the insulated quadrant of a Dolezalek electrometer, and was initially at earth potential.

Fig. 2.



This arrangement of gauzes effectively screened A from any ions generated in the gap EF. No ions from the space above M could possibly penetrate to A owing to the arrangement of the electric fields. Moreover, owing to the relative distances of N from M and A, it is exceedingly unlikely that any photo-electrons emitted by N could arrive at A. It may therefore be assumed that, when a discharge was passing from E to F, any current passing from N to A was due to ionization of the gas in the vicinity of N or A.

The discharge between E and F was produced by means of an induction-coil used in conjunction with a motor mercury-jet interrupter. Every precaution was taken to render the action of the coil reliable. The mean current (secondary) was measured by means of a delicate meter, reading to about 600 microamperes. The average current between E and F was about 200 microamperes.

The other measurements necessary were of pressure and ionization current. The former was read from an ordinary barometer tube pressure gauge. This was sufficiently accurate for the purpose. The ionization current was measured by means of a Dolezalek electrometer. Since the currents were very large—of the order of 10^{-12} ampere—a phosphor-bronze suspension was used, the sensitivity of which was 10 mm. to the volt with the scale at 1 m. distance. It was necessary that the sensitivity should remain very constant; this was verified on numerous occasions.

Variation of Ionization Current with Discharge Current, the Pressure remaining Constant.

Both the gas and the tube being so dry as to give no indication of impurity when the aforementioned tests were carried out, the discharge-tube was filled with hydrogen to atmospheric pressure. A small current was then passed through the gas, and it was verified that the ionization current remained constant to 1 per cent. of its value over a large number of readings. To avoid any progressive effects due to temperature changes, a 10 minutes' pause was allowed after each reading, and the readings were taken in a definite order. Starting with a discharge current of about 50 microamperes, readings were taken at 50, 100, 150, . . 500, 500, . . 150, 100, 50. Usually, owing to temperature variations, and perhaps to a very small unexamined change in the gas, the readings taken with decreasing discharge current were slightly greater (maximum difference, 2 per cent.) than those taken with the discharge current increasing. Then the pressure of the gas was reduced to about 60 cm. of mercury, and the same series of readings was taken. In general, as the pressure was reduced, it became necessary to reduce the maximum discharge current, since the ionization became too large for accurate measurement. Thus, at about 30 cm. the maximum discharge current was 150 microamperes. In fig. 3 the results of these experiments are shown. The abscissa measures the discharge current; the ordinate the ionization current. The curves are drawn for different pressures in the same sample of gas.

Discussion of the Results.

The curves shown in fig. 3 are typical of all the samples of gas which were used. The absolute value of the ionization current at a given pressure and for a given discharge current varied slightly from sample to sample; but the shapes of the curves did not so vary. It is claimed that they are typical of the gas hydrogen.

Suppose that the source of the radiation (the discharge) is at the point A, and the ionization current which was observed takes place in the region B. Then, so long as the pressure of the gas is not varied, the ionization is a measure of the intensity of the radiation at B. Also, so long as the pressure is not varied, the absorption of the radiation between its source A and the point B remains constant, and hence the ionization current at B is a measure of the intensity of the radiation *at its source* A. The only assumption made here is that the quality of the radiations does not vary as the discharge current is varied. Therefore the shape of any particular curve in fig. 3 exhibits the mode of variation of the intensity of the radiation from the discharge as the current in the latter is varied.

It is evident from a casual examination of the curves that, the pressure remaining constant, the radiation intensity increases in a *roughly* linear manner with the discharge current. This had already been observed *.

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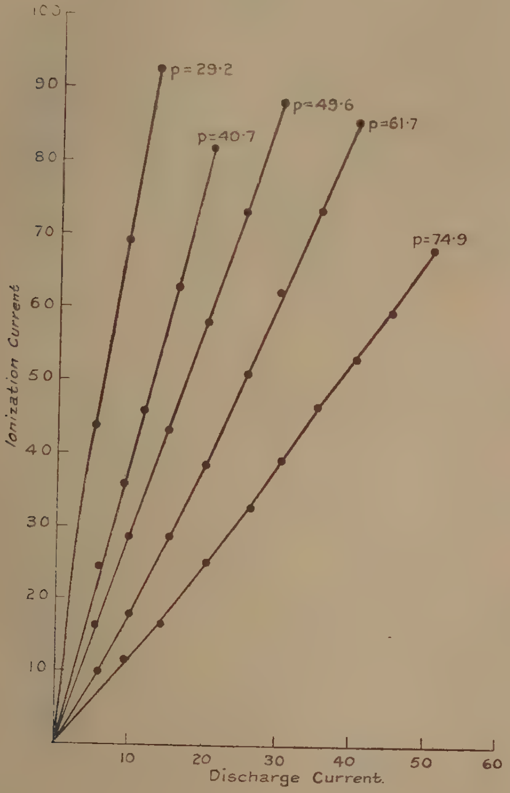
* *Loc. cit.*

A more careful examination of the curves leads to more definite and more interesting conclusions. The curves, as shown in the figure, have been drawn to pass through the origin, since the radiation intensity must be zero when the discharge current is zero.

Fig 3.



The curves at 74·9 and 61·7 cm. of mercury have a small but definite concavity upwards; the two curves obtained at 49·6 and 40·7 cm. are almost straight lines; the curve at 29·2 cm. is slightly convex upwards. Also, in three of the four curves taken at high pressures the point representing the radiation intensity at lowest discharge current lies above the curve through the origin. These are all real phenomena of the gas; they are shown in all the curves which have been taken.

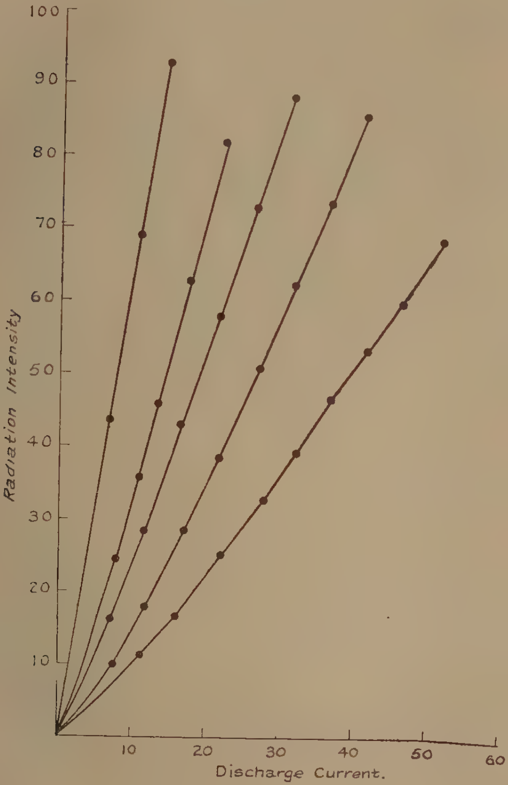
The results can be reduced to order in a very simple manner. If the origin is taken about two discharge-current units to the left of the origin shown in fig. 3, the curves become very much simplified. The anomalous points now lie on the curves; the curves all show a tendency to concavity upwards; and the concavity, or variation from a straight line, decreases uniformly as the pressure of the gas is reduced. Is there, then, any reason for believing that the true origin of coordinates lies a little to the left of the origin given by the amperemeter?

The current measured by the meter should be the mean current through the secondary of the coil. The current in the coil varies in a periodic fashion; if this current is represented by c, the current measured by the meter should be proportional to $i=\frac{1}{T}\int_0^T c\,dt$, and i should be accurately proportional to c. But even under the best conditions there is always a certain amount of "inverse current" in the secondary circuit. This current is sufficient to produce a very small discharge, and its direction is opposite to that of the current at "break." Hence it is to be *expected* that the current measured by the meter should be less than the true mean current by a small quantity. Under the conditions of the experiment this quantity would seem to have been of the order of two units.

That this inverse current was present was shown by a very interesting experiment. The current flowing in the discharge was reduced by means of a series resistance in the primary circuit. As the current fell to zero, it was observed that the discharge was still just visible in the dark. On increasing the resistance in the primary circuit, the meter actually showed a small negative deflexion due to inverse current. The explanation is to be found in the fact that, while the current at "break" depends upon the current flowing in the primary circuit (which was reduced by adding resistance), the inverse current at "make" depends upon the total E.M.F. across the primary circuit (which was not varied by adding resistance). By using a large series resistance in the primary circuit it is possible to make the inverse current as large as the current at "break."

Fig. 4 shows the corrected curves for the variation of radiation intensity with discharge current. The curves have again been made to pass through the origin. They will now be considered in detail.

Fig. 4.



All the curves can be represented by the expression.

$$I=k_1 i+k_2 i^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I is the radiation intensity (ionization current) and i is the discharge current, k_1 and k_2 being constants.

Evaluation of k_1 and k_2 for the curve taken at 74·9 cm. of mercury leads to the expression

$$I=K(200\,i+i^2), \quad \text{or} \quad \frac{k_1}{k_2}=200.$$

This value is characteristic of the curves taken about atmospheric pressure. The curves obtained at lower pressures are amenable to the same treatment, but, as the pressure is reduced, k_2 tends to zero—the curves become straight lines.

Theoretical Interpretation of the Results.

The use of the corrected values for the secondary current gives a measure of the total current flowing in the discharge, and it has been found that the radiation intensity is proportional to the sum of two quantities proportional to the total current and to the square of the total current. It might be suggested that the two terms in equation (1) represent a second approximation to a function which could be expressed as an infinite series in powers of i. The writer is not inclined to accept this suggestion.

Radiation from a discharge may arise from two principal causes: it may be emitted by the processes following inelastic impact

(i.) between an ion and a neutral molecule, or

(ii.) between two ions.

Assuming that the pressure is constant, and that the field of electric force in the gap is not affected to any extent by variation in the discharge current, then the probability of radiation arising from the impact of ions on neutral molecules will be proportional to the number of ions in the gap, that is

$I=k_1\,i$, where I, k_1, i have their usual meanings.

Making the same assumptions, the probability of radiation arising from the impact of ions with ions will be proportional to the product of the number of ions of either sign in the gap, that is

$I=k_2 i^2$, where k_2 is again a constant.

Hence, if the ionizing radiation is emitted by both processes in the discharge, the intensity will be given by the expression

$$I=k_1\,i+k_2\,i^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which is the expression already found empirically for the experimental curves.

If the above hypothesis be assumed, it may be concluded that the experiments show that the greater part of the ionizing radiation emitted by the discharge has its source in the impact of ions with neutral molecules. When the pressure is high, a small proportion of the radiation is due to purely ionic impact; but, as the pressure is diminished, these ionic impacts become of smaller relative importance. When the pressure is less than half an atmosphere, it is estimated that less than one-thousandth of the radiation intensity is due to this source.

It is a matter of some difficulty to classify in the category of arc or spark a discharge such as that which has just been discussed. The true arc takes place at a relatively low potential, the true spark at a very much higher potential. The evidence of the rotating mirror has shown that the discharge under consideration is a mixture of both phenomena. A high potential spark is followed by a number of low potential arcs. This is particularly the case at high pressures, where the conductivity of the gas is least. As the pressure diminishes, the arc begins to predominate, until the discharge degenerates into its typical low-pressure form. Thus the evidence of other investigations confirms the result arrived at in the present paper by means of the new hypothesis, since the arc radiation is chiefly emitted by neutral atoms or molecules, while the spark radiation is typical of the interaction of ions.

Experimental Verification of the New Hypothesis.

The hypothesis put forward in the above analysis appears to be sufficiently important to justify exhaustive tests of its validity being made. The writer has carried out a rough test * for a glow discharge.

A neon glow lamp such as is supplied for spectroscopic work was used as the discharge. The current was measured by a milliamperemeter (0–5 milliamp.). The detector of the radiation (visible) was a photoelectric cell supplied by the General Electric Co. (Type KMV6—this is a vacuum cell, the cathode being a monomolecular layer of potassium on copper oxide). The method of measuring the photoelectric current was suggested by Professor Crowther, and is certainly worth description. The circuit is shown diagrammatically in fig. 5.

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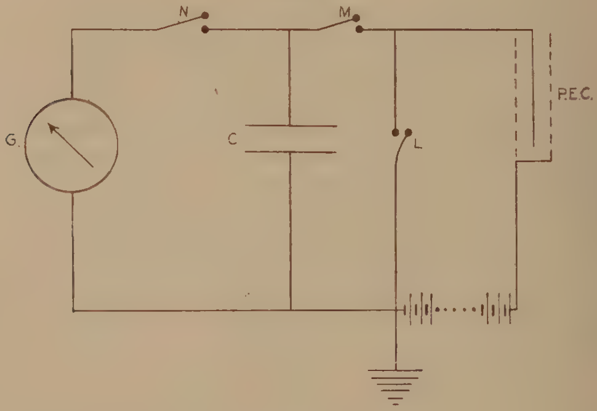
* At the University of Reading.

P.E.C. represents the cell, L, M, N are well-insulated keys, C is a capacity of about 1μ F., and G is a ballistic galvanometer. When the cell is exposed to light, the cathode is connected to the capacity which is allowed to charge up for a given time. It is then discharged through the galvanometer and the deflexion noted.

Fig. 5.



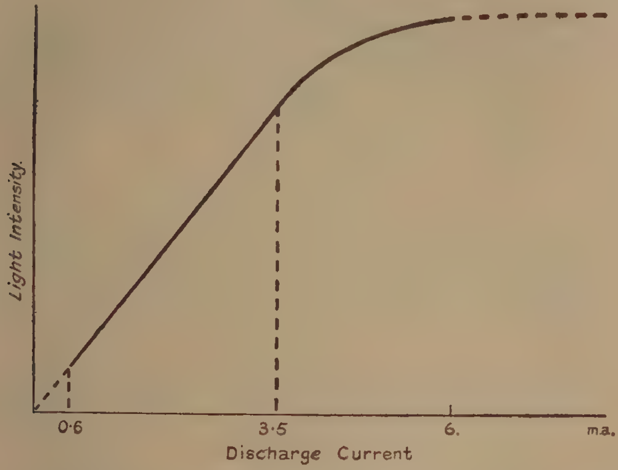
The method has many advantages :—

1. The measuring instrument is a robust galvanometer which need not be particularly sensitive.
2. So long as the insulation of the condenser is good, there is no limit to the sensitivity of the method ; the galvanometer deflexion varies directly as the time of charge.
3. The potential of the cathode, which is also the potential difference across the condenser, need never rise above 0·1 volt.

In the particular experiment carried out by the writer the photoelectric current was of the order 10^{-12} ampere. The galvanometer sensitivity was about 240 mm. per microcoulomb ; the time of charge was 30 sec. and, of course, large deflexions were obtained. This method for the measurement of reasonably large ionization or photoelectric currents is, in the opinion of the writer, superior to any form of electrometer.

The photoelectric cell was first calibrated. It was found that with 120 volts across the cell the current was accurately proportional to the light intensity. Then the neon lamp was set up in the vicinity of the cell and the p.e. current was measured for discharge currents from 0·5 to 6·0 milliamp. The full line in fig. 6 represents a typical result.

Fig. 6.



The dotted line is the suggested form of the curve outside the limits of observation.

It will be seen immediately that the curve is in complete agreement with the writer's hypothesis. Practically all the light from such a neon glow is due to the *arc* radiation from the gas. The curve of light intensity against discharge current is a straight line from 0 to 3·5 milliamp. A saturation intensity appears to be reached at about 5 milliamp.

When the current is small, the theory given above is completely verified. When the current is such, however, that the number of ions in the gap is of the same order as the number of gas molecules in the gap, the light intensity will begin to depend also upon the number of the latter.

Ultimately a stage will be reached where the light intensity will be proportional to the number of neutral molecules, and thus a saturation intensity will appear. The value of the discharge current, i, at which the light intensity becomes saturated will be a function only of the pressure of the gas. If it were possible to try the experiment with the same lamp at different gas pressures, i should be found to vary directly as the pressure of the gas.

The writer has not found it possible to pursue the investigation further, or to try the same experiment with a typical "spark" source. If the experiment were performed in the best way, monochromatic light would be used with some form of optical photometer. Should the hypothesis be found to conform to such a test, it might be possible, where the light intensity was sufficiently great, to utilize it to investigate the ultimate source of discharge spectral lines.

Summary.

1. Experiments are described which strongly suggest that the ionizing radiations emitted by point discharges in hydrogen emanate from the gas itself.

2. The mode of variation of the intensities of these radiations with the current flowing in the discharge is set forth.

It is suggested that the intensity of arc radiation from a discharge varies directly as the discharge current, and that the intensity of spark radiation varies as the square of the current.

The results of the present experiments are discussed with reference to this hypothesis.

3. A rough test of the hypothesis is described.

The greater part of the above work was performed in the research laboratories of the Natural Philosophy Department of Glasgow University, and the writer wishes once again to express his gratitude to Professor Taylor Jones for his advice and encouragement. The test of the hypothesis was carried out in the Physics Department of the University of Reading, and the writer's thanks are due to Professor Crowther, who suggested the method of measuring the photoelectric current which is described above.

Reading,
October, 1929.

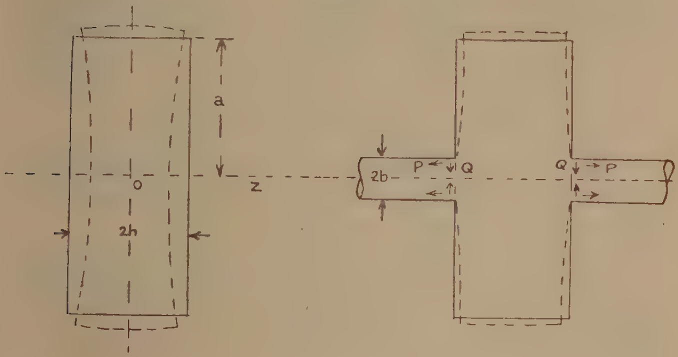
CIII. *The Effect of Axial Restraint on the Stress in a Rotating Disk.* By Walter G. Green, *Ph.D.*[*]

[Thesis approved for the Degree of Doctor of Philosophy in the University of London.]

§ 1. Introduction.

THE problem under consideration is that of a rotating disk carried on a shaft. The effect of the presence of the shaft is to check the movements in the direction of the axis, of parts of the disk that are near the axis. The restraint may be effected in various ways. The solution, in which a disk of outer radius a, and of thickness $2h$, is restrained by concentrated axial tensions P, induced by rotation, at the centres of the outside faces, has already been given[†].

Fig. 1.



A further development of this analysis can be obtained by representing the shaft as equivalent to symmetrical distributions of normal and tangential surface tractions acting on the outside faces of the disk, and symmetrical about its axis.

Consider, then, a disk of outer radius a and of thickness $2h$, the plane faces being represented by $z = \pm h$. When the disk rotates with angular velocity ω, and is restrained in the manner indicated, two stress-systems will result, viz.:

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[*] Communicated by the Author.

[†] Phil. Mag. i. no. 6, p. 1236 (1926).

(A) That due to symmetrical distributions of traction in a complete disk at rest.

(B) That due to rotation ω in a complete disk under no superficial tractions *.

For the first, although it is necessary to regard the radius of the disk as infinite, the results obtained show that the error due to this assumption is negligible.

Before developing the analysis, it will be necessary to glance at the problem of finding the stress-components and displacements produced at the surface of a semi-infinite solid by various distributions of traction applied at the plane boundary. This is Boussinesq's problem †.

The effects of symmetrical distributions of normal and tangential surface tractions will be considered separately.

§ 2. SYMMETRICAL DISTRIBUTION OF NORMAL TRACTION ABOUT A POINT ON A PLANE BOUNDARY.

For symmetrical strain in a solid of revolution ‡ the results may be expressed in terms of a function χ which satisfies the differential equation $\nabla^4\chi=0$, where

$$\nabla^2\chi\equiv\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}\right)\equiv\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}\right).$$

The stress-components are then given by

$$\left.\begin{aligned}\widehat{rr}&=\frac{\partial}{\partial z}\left[\sigma\,.\,\nabla^2\chi-\frac{\partial^2\chi}{\partial r^2}\right]\\ \widehat{\theta\theta}&=\frac{\partial}{\partial z}\left[\sigma\,.\,\nabla^2-\frac{1}{r}\,.\frac{\partial\chi}{\partial r}\right]\\ \widehat{zz}&=\frac{\partial}{\partial z}\left[(2-\sigma)\nabla^2\chi-\frac{\partial^2\chi}{\partial z^2}\right]\end{aligned}\right\}, \quad . \quad . \quad . \quad . \qquad (1)$$

$$\widehat{zr}=\frac{\partial}{\partial r}\left[(1-\sigma)\nabla^2\chi-\frac{\partial^2\chi}{\partial z^2}\right], \quad . \quad . \quad . \qquad (2)$$

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* For this Chree's solution is taken. See A. E. H. Love, 'Mathematical Theory of Elasticity,' 3rd Ed. § 102, case *b*.

† H. Lamb, Proc. Lond. Math. Soc. xxxiv. p. 276 (1902).

‡ Love, *op. cit.* § 188.

and the displacements by

$$\left.\begin{aligned} u &= -\frac{1+\sigma}{\mathrm{E}}\cdot\frac{\partial^2\chi}{\partial r\partial z}, \\ w &= \frac{1+\sigma}{\mathrm{E}}\cdot\left[(1-2\sigma)\nabla^2\chi + \frac{1}{r}\frac{\partial}{\partial r}\cdot r\cdot\frac{\partial\chi}{\partial r}\right]. \end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

Suppose $z=0$ to be the bounding plane, the positive direction of the axis of z to be that which passes into the interior of the body, then, for a normal distribution of traction at the surface, symmetrical about the axis of z, we can write

$$\chi = \int_0^\infty \frac{\phi_1(k)}{k^3}\left[\{(2\sigma+kz)\}\mathrm{J}_0(kr)e^{-kz} - \{2\sigma+kz(1-2\sigma)\}\right]dk, \quad . \quad (4)$$

where

$$\nabla^2\chi = -\int_0^\infty \frac{2\phi_1(k)}{k}\cdot e^{-kz}\mathrm{J}_0(kr)\,dk. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The nature of the distribution of normal traction depends on $\phi_1(k)$, a function of k, which is, as yet, arbitrary.

The stress-components then become

$$\left.\begin{aligned} \widehat{rr} &= \int_0^\infty \phi_1(k)e^{-kz}\left[2\sigma\frac{\mathrm{J}_1(kr)}{kr} + \left\{\mathrm{J}_0(kr) - \frac{\mathrm{J}_1(kr)}{kr}\right\}(1 \quad kz)\right]dk, \\ \widehat{\theta\theta} &= \int_0^\infty \phi_1(k)e^{-kz}\left[\frac{\mathrm{J}_1(kr)}{kr}\cdot(1-kz) + 2\sigma\left\{\mathrm{J}_0(kr) - \frac{\mathrm{J}_1(kr)}{kr}\right\}\right]dk, \\ \widehat{zz} &= \int_0^\infty \phi_1(k)\,.\,e^{-kz}\,.\,(1+kz)\,.\,\mathrm{J}_0(kr)\,dk. \end{aligned}\right\} \quad . \quad . \quad . \quad (6)$$

$$\widehat{zr} = \int_0^\infty \phi_1(k)\,.\,e^{-kz}\,.\,kz\mathrm{J}_1kr(dk), \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and the displacements are given by

$$\left.\begin{aligned} w &= -\frac{(1+\sigma)}{\mathrm{E}}\int_0^\infty \frac{\phi_1(k)}{k}\,.\,e^{-kz}\,.\,\{2(1-\sigma)+kz\}\mathrm{J}_0(kr)\,dk, \\ u &= \frac{(1+\sigma)}{\mathrm{E}}\int_0^\infty \frac{\phi_1(k)}{k}\,e^{-kz}\,.\,\{(1-2\sigma)-kz\}\mathrm{J}_1(kr)\,dk, \end{aligned}\right\} \quad . \quad . \quad . \quad (8)$$

when $z=0$ we have

$$\left.\begin{aligned}\widehat{zz} &= \int_0^\infty \phi_1(k)\,.\,J_0(kr)dk,\\ \widehat{zr} &= 0,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (9)$$

the surface displacements being given by

$$\left.\begin{aligned}w &= \frac{-2(1-\sigma^2)}{E}\int_0^\infty \frac{\phi_1(k)}{k}\,J_0(kr)\,.dk,\\ u &= \frac{(1-2\sigma)(1+\sigma)}{E}\int_0^\infty \frac{\phi_1(k)}{k}\,J_1(kr)dk\end{aligned}\right\} \quad . \quad . \quad (10)$$

To make equation (9) represent any desired distribution of normal traction, let ρ be the radius vector and b the limiting radius of the area to which traction is applied, then we must write

$$\phi_1(k)=k\int_0^b f(\rho)J_0(k\rho)\,.\,\rho\,.\,d\rho, \quad . \quad . \quad . \quad (11)$$

where $f(\rho)$ is the given surface value of $\widehat{zz}$. Some special cases are outlined below :—

(a) *Tension at a Point on a Plane Boundary.*

If the origin is the point at which a total load P is applied then

$$\phi_1(k)=\frac{P\,.\,k}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where P is positive for tension. The stress-components at the boundary become

$$\left.\begin{aligned}\widehat{rr} &= -\frac{P}{2\pi r^2}\,.\,(1-2\sigma)\\ \widehat{\theta\theta} &= \frac{P}{2\pi r^2}\,.\,(1-2\sigma)\end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (13)$$

and the surface displacements are

$$\left.\begin{aligned}w &= -\frac{P}{\pi r}\,.\,\frac{(1-\sigma^2)}{E}\\ u &= \frac{P}{\pi r}\,.\,\frac{(1-2\sigma)(1+\sigma)}{2E}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (14)$$

(b) *Total Load P uniformly distributed round a circumference of radius* b.

Here we may suppose that $f(\rho)$ vanishes at all radii except when $r=b$. Hence,

$$\phi_1(k)=\frac{P\,.\,k}{2\pi}J_0(kb), \quad . \quad . \quad . \quad . \qquad (15)$$

substituting in equations (6), when $z=0$, and integrating, it can be shown that for values of $r<b$, $\widehat{rr}$ and $\theta\theta$ are both zero. When $r=b$ the integrals become infinite, and finally, for values of $r>b$, the surface values of the stress-components are the same as if P were concentrated at the centre of the circle, and are given by equations (13).

Again, substituting in equations (10), and integrating [*], the corresponding surface displacements are given by

$$\left.\begin{aligned} w&=-\frac{P}{\pi E}\frac{(1-\sigma^2)}{b}\cdot{}_2F_1\left(\frac{1}{2},\frac{1}{2};1;\frac{r^2}{b^2}\right),\\ u&=0\end{aligned}\right\}r<b. \quad . \qquad (16)$$

$$\left.\begin{aligned} w&=-\frac{P}{\pi E}\frac{(1-\sigma^2)}{r}\cdot{}_2F_1\left(\frac{1}{2},\frac{1}{2};1;\frac{b^2}{r^2}\right),\\ u&=\frac{P}{\pi E}\cdot\frac{(1-2\sigma)(1+\sigma)}{2r}\end{aligned}\right\}r>b. \quad . \qquad (17)$$

Applying Gauss's Theorem for the Hypergeometric Function when $r=b$, w becomes infinite. For values of $r>b$, u is the same as if P were concentrated.

(c) *Symmetrical Distribution of Normal Traction varying as* ρ^{n-1}.

For a total load P we have

$$f(\rho)=(n+1)\cdot\frac{P}{2\pi b^2}\left(\frac{\rho}{b}\right)^{n-1}. \quad . \quad . \quad . \quad . \qquad (18)$$

---

[*] G. N. Watson, 'Theory of Bessel Functions'; u comes from Weber's Result, p. 406, Case 8; w from Gubler's Integral. The displacement w, given by equations (16) and (17), is also expressible in the form, $w=-\frac{P}{\pi E}\cdot\frac{1-\sigma^2}{\pi}\cdot\frac{2K}{(r+b)}$, where the modulus of the complete elliptic integral K is $\frac{2\sqrt{rb}}{(r+b)}$.

Hence, from equation (11).

$$\phi_1(k)=\frac{Pk}{2\pi}\cdot\frac{n+1}{b^{n+1}}\int_0^b \rho^n\,.\,J_0(k\rho)\,.\,d\rho. \quad . \quad . \quad (19)$$

Here the surface displacements can be obtained by direct integration of the results given in case *b* above.

Thus,

$$\left.\begin{aligned} w&=-\frac{(1-\sigma^2)}{E}\frac{P}{\pi}\frac{n+1}{b^{n+1}}\cdot\Bigg[\int_r^b \rho^{n-1}\,.\,{}_2F_1\left(\frac{1}{2},\frac{1}{2};1;\frac{r^2}{\rho^2}\right)d\rho \\ &\qquad+\int_0^r \frac{\rho^n}{r}\,.\,{}_2F_1\left(\frac{1}{2},\frac{1}{2};1;\frac{\rho^2}{r^2}\right)d\rho\Bigg], \\ u&=\frac{(1-2\sigma)(1+\sigma)}{E}\cdot\frac{P}{2\pi b}\cdot\left(\frac{r}{b}\right)^n; \end{aligned}\right\}$$

$$r<b. \quad . \quad . \quad (20)$$

$$\left.\begin{aligned} w&=-\frac{(1-\sigma^2)}{E}\cdot\frac{P}{\pi}\frac{n+1}{b^{n+1}}\cdot\int_0^b \frac{\rho^n}{r}\,.\,{}_2F_1\left(\frac{1}{2},\frac{1}{2};\;1;\;\frac{\rho^2}{r^2}\right)d\rho, \\ u&=\frac{(1-2\sigma)(1+\sigma)}{E}\cdot\frac{P}{2\pi r}; \end{aligned}\right\}$$

$$r>b \quad . \quad . \quad (21)$$

when $r=0$ equation (20) gives

$$w=-\frac{(1-\sigma^2)}{E}\cdot\frac{P}{\pi b}\cdot\frac{n+1}{n}, \quad . \quad . \quad . \quad (22)$$

and the corresponding displacement at the edge of the circle is

$$\begin{aligned} w=-\frac{(1-\sigma^2)}{E}\cdot\frac{P}{\pi b}\Bigg\{1&+\left(\frac{1}{2}\right)^2\frac{n+1}{n+3} \\ &+\left(\frac{1\,.\,3}{2\,.\,4}\right)^2\frac{n+1}{n+5}+\dots\Bigg\}. \quad . \quad . \quad (23) \end{aligned}$$

From equations 6, when $z=0$, the values of the stress-components at the boundary become

$$\left.\begin{aligned} \widehat{rr}&=\frac{P}{2\pi b^2}\cdot(n+2\sigma)\,.\left(\frac{r}{b}\right)^{n-1}, \\ \widehat{\theta\theta}&=\frac{P}{2\pi b^2}(2n\sigma+1)\,.\left(\frac{r}{b}\right)^{n-1}, \\ \widehat{zz}&=\frac{P}{2\pi b^2}\cdot(n+1)\,.\left(\frac{r}{b}\right)^{n-1}. \end{aligned}\right\}^{*} r<b. \quad . \quad (24)$$

---

* Equations (6), when $z=0$, involve integrals shown in equations (9) and (10). The stress-components are therefore readily evaluated.

For values of $r > b$ the stress-components are given by equations (13) as before.

(d) *Uniform Distribution of Normal Traction.*

For a total load P, uniformly distributed over the circular area of radius b, put $n=1$ in equation (19). This gives

$$\phi_1(k) = \frac{P}{\pi b} \cdot J_1(kb). \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The surface values of the stress-components are then obtained by putting n equal to unity in equations (24).

For the displacements at the boundary, equations (10) become

$$\left. \begin{aligned} w &= -2\frac{(1-\sigma^2)}{E} \cdot \frac{P}{\pi b} \cdot {}_2F_1\left(\frac{1}{2}, -\frac{1}{2};\ 1\ ;\ \frac{r^2}{b^2}\right), \\ u &= \frac{(1-2\sigma)(1+\sigma)}{E} \cdot \frac{P}{\pi b^2} \cdot \frac{r}{2}; \end{aligned} \right\} r < b \qquad (26)$$

$$\left. \begin{aligned} w &= -\frac{(1-\sigma^2)}{E} \cdot \frac{P}{\pi r} \cdot {}_2F_1\left(\frac{1}{2}, \frac{1}{2};\ 2\ ;\ \frac{b^2}{r^2}\right), \\ u &= \frac{(1-2\sigma)(1+\sigma)}{E} \cdot \frac{P}{2\pi r}. \end{aligned} \right\} r > b. \qquad (27)$$

Applying the Gaussian formula for ${}_2F_1$ $(\alpha, \beta, \gamma, 1)$, the axial displacement at the edge of the circle is given by

$$w = -\frac{(1-\sigma^2)}{E} \cdot \frac{P}{\pi b} \cdot \frac{4}{\pi}. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

§ 3. SYMMETRICAL DISTRIBUTION OF TANGENTIAL SURFACE TRACTION ABOUT A POINT ON A PLANE BOUNDARY.

Using the notation outlined in the previous article, then, for a distribution of tangential surface traction, symmetrical about the axis of z, we can write

$$\chi = \int_0^\infty \frac{\phi_2(k)}{k^3} [\{(1-2\sigma) - kz\} J_0(kr) e^{-kz} \\ - \{(1-2\sigma) - 2kz(1-\sigma)\}] dk, \quad . \quad (29)$$

where

$$\nabla^2 \chi = \int_0^\infty \frac{2\phi_2(k)}{k} \cdot e^{-kz} \cdot J_0(kr) dk. \quad . \quad . \quad . \quad (30)$$

The nature of the distribution depends on $\phi_2(k)$, a function of k, which is, as yet, arbitrary.

The stress-components may then be written

$$\left.\begin{aligned}
\widehat{rr} &= -\int_0^\infty \phi_2(k)e^{-kz}\Big[2\sigma\,.\,\frac{J_1(kr)}{kr} \\
&\qquad\qquad + \Big\{J_0(kr)-\frac{J_1(kr)}{kr}\Big\}(2-kz)\Big]dk, \\
\widehat{\theta\theta} &= -\int_0^\infty \phi_2(k)e^{-kz}\Big[\frac{J_1(kr)}{kr}(2-kz) \\
&\qquad\qquad + 2\sigma\Big\{J_0(kr)-\frac{J_1(kr)}{kr}\Big\}\Big]dk, \\
\widehat{zz} &= -\int_0^\infty \phi_2(k)e^{-kz}\,.\,kz\,.\,J_0(kr)dk.
\end{aligned}\right\} \quad . \; . \; . \quad (31)$$

$$\widehat{zr} = \int_0^\infty \phi_2(k)e^{-kz}\,.\,(1-kz)\,.\,J_1(kr)dk, \quad . \; . \; . \; . \quad (32)$$

and the displacements become

$$\left.\begin{aligned}
w &= \frac{1+\sigma}{E}\int_0^\infty \frac{\phi_2(k)}{k}\,.\,e^{-kz}\{2(1-\sigma)-(1-kz)\}J_0(kr)\,.\,dk, \\
u &= -\frac{1+\sigma}{E}\int_0^\infty \frac{\phi_2(k)}{k}\,.\,e^{-kz}\{(1-2\sigma)+(1-kz)\}J_1(kr)dk,
\end{aligned}\right\} \quad . \; . \; . \quad (33)$$

when $z=0$ we have

$$\left.\begin{aligned}
\widehat{zz} &= 0, \\
\widehat{zr} &= \int_0^\infty \phi_2(k)J_1(kr)\,.\,dk,
\end{aligned}\right\}, \quad . \; . \; . \quad (34)$$

the surface displacements being given by

$$\left.\begin{aligned}
w &= \frac{(1-2\sigma)(1+\sigma)}{E}\int_0^\infty \frac{\phi_2(k)}{k}\,.\,J_0(kr)dk, \\
u &= -2\frac{(1-\sigma^2)}{E}\int_0^\infty \frac{\phi_2(k)}{k}J_1(kr)dk.
\end{aligned}\right\}. \quad . \quad (35)$$

To make equation (34) represent any desired distribution of tangential surface traction we must write

$$\phi_2(k) = k\int_0^b f(\rho)J_1(k\rho)\,.\,\rho\,.\,d\rho, \quad . \; . \; . \quad (36)$$

where ρ and b have the same meanings as in equation (11), and $f(\rho)$ is the given surface value of $\widehat{zr}$. Some special cases are outlined below.

(a) *Total Tangential Surface Traction Q, uniformly distributed round a Circumference of Radius* b.

Here we may suppose that $f(\rho)$ vanishes at all radii, except when $r=b$. Hence,

$$\phi_2(k) = \frac{k}{2\pi} J_1(kb) \,.\int_0^b f(\rho)\,.\,2\pi\rho\,.\,d\rho,$$

or

$$\phi_2(k) = \frac{Qk}{2\pi}\,.\,J_1(kb). \qquad (37)$$

Substituting in equations (35) the surface displacements are given by *

$$\left.\begin{aligned} w &= \quad \frac{Q}{\pi b}\,.\,\frac{(1-2\sigma)(1+\sigma)}{2E}, \\ u &= -\frac{Q}{2\pi}\,.\,\frac{r}{b^2}\,.\,\frac{(1-\sigma^2)}{E}\,.\,{}_2F_1\left(\frac{3}{2},\frac{1}{2};\ 2\ ;\ \frac{r^2}{b^2}\right); \end{aligned}\right\} r<b, \qquad (38)$$

$$\left.\begin{aligned} w &= \quad 0, \\ u &= -\frac{Q}{2\pi}\,.\,\frac{b}{r^2}\,.\,\frac{(1-\sigma^2)}{E}\,.\,{}_2F_1\left(\frac{3}{2},\frac{1}{2};\ 2\ ;\ \frac{b^2}{r^2}\right), \end{aligned}\right\} r>b. \qquad (39)$$

Examining the displacements when $r=b$, as previously indicated, it is seen that u becomes infinite, and w is given by

$$w = \frac{Q}{2\pi b}\,.\,\frac{(1-2\sigma)(1+\sigma)}{2E}.$$

(b) *Symmetrical Distribution of Tangential Surface Traction varying as ρ^n.*

Writing $f(\rho) = (n+2)\dfrac{Q}{2\pi b^2}\left(\dfrac{\rho}{b}\right)^n$, the surface displacements may be obtained by direct integration of the results given in case *a* above.

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* w comes from Weber's Result, and u from Gubler's Integral. G. N. Watson, *op. cit.* p. 406, Case 8; and p. 410.

Thus

$$\left.\begin{aligned} w &= \frac{n+2}{n+1}\cdot\frac{Q}{\pi b}\cdot\frac{(1-2\sigma)(1+\sigma)}{2E}\left\{1-\left(\frac{r}{b}\right)^{n+1}\right\}, \\ u &= -\frac{(1-\sigma^2)}{E}\cdot\frac{Q}{2\pi}\frac{n+2}{b^{n+2}} \\ &\quad \times\left[\int_r^b \rho^{n-1}\,.\,r\,{}_2F_1\left(\frac{3}{2},\frac{1}{2};\,2\,;\,\frac{r}{\rho^2}\right)d\rho,\right. \\ &\quad \left.+\int_0^r \frac{\rho^{n+2}}{r^2}\,{}_2F_1\left(\frac{3}{2},\frac{1}{2};\,2\,;\,\frac{r^2}{\rho^2}\right)d\rho\right]; \end{aligned}\right\}\ r<b. \quad (40)$$

$$\left.\begin{aligned} w &= 0, \\ u &= -\frac{(1-\sigma^2)}{E}\cdot\frac{Q}{2\pi}\cdot\frac{n+2}{b^{n+2}} \\ &\quad \times\int_0^b \frac{\rho^{n+2}}{r^2}\,{}_2F_1\left(\frac{3}{2},\frac{1}{2};\,2\,;\,\frac{\rho^2}{r^2}\right)d\rho. \end{aligned}\right\}\ r>b. \quad (41)$$

At the edge of the circle, the radial displacement is then given by

$$u=-\frac{(1-\sigma^2)}{E}\cdot\frac{Q}{2\pi b}\cdot\frac{n+2}{n+3}\left\{1+\frac{3}{2}\left(\frac{1}{2}\right)^2\frac{n+3}{n+5}\right.$$
$$\left.+\frac{5}{3}\left(\frac{1\,.\,3}{2\,.\,4}\right)^2\frac{n+3}{n+7}+\ldots\right\}. \quad . \quad (42)$$

(c) *Symmetrical Distribution of Surface Traction varying as the Radius.*

For a total tangential surface traction Q we have

$$f(\rho)=\frac{3Q}{2\pi b^2}\cdot\frac{\rho}{b},$$

so that equation (36) becomes

$$\phi_2(k)=\frac{3Q}{2\pi b}\cdot J_2(kb). \quad . \quad . \quad . \quad . \quad (43)$$

For the surface displacements we then find

$$\left.\begin{aligned} w &= \frac{3Q}{2\pi b}\frac{(1-2\sigma)(1+\sigma)}{2E}\left\{1-\frac{r^2}{b^2}\right\}^*, \\ u &= -\frac{3Q}{2\pi b}\cdot\frac{r}{b}\cdot\frac{(1-\sigma^2)}{E}\cdot{}_2F_1\left(\frac{3}{2},-\frac{1}{2};\,2\,;\,\frac{r^2}{b^2}\right); \end{aligned}\right\} r<b, \quad (44)$$

---

* These integrals are particular cases of the Weber and Schafheitlin integral (see G. N. Watson, *op. cit.* § 13.41, p. 404, equations (4) and (5)). In deducing the displacement w, it will be noticed that ${}_2F_1\left(1,-1\,;\,1\,;\,\frac{r^2}{b^2}\right)=\left(1-\frac{r^2}{b^2}\right)$. Equation (7), p. 404, shows the limiting values of the integrals when $r=b$.

$$\left.\begin{aligned} w &= 0, \\ u &= -\frac{3Q}{2\pi b}\cdot\frac{b^2}{4r^2}\,\frac{(1-\sigma^2)}{E}\cdot{}_2F_1\left(\frac{3}{2},\frac{1}{2};\;3\;;\;\frac{b^2}{r^2}\right)^{*}. \end{aligned}\right\} r > b. \quad (45)$$

At the edge of the circle, the surface displacements become

$$\left.\begin{aligned} w &= 0, \\ u &= -\frac{Q}{\pi b}\cdot\frac{1-\sigma^2}{E}\cdot\frac{2}{\pi}. \end{aligned}\right\}. \quad . \quad . \quad . \quad (46)$$

§ 4. The Stress-System (A), due to a Symmetrical Distribution of Normal Traction, in a Complete Disk at Rest.

(a) This system is made up of three component systems, viz.:

I. That due to symmetrical distributions of traction, acting at the surface of an infinite solid, bounded by the plane $z=-h$, and lying on the side $z>-h$ of this plane.

II. That due to symmetrical distributions of traction, acting at the surface of an infinite solid, bounded by the plane $z=h$, snd lying on the side $z<h$ of this plane.

III. The system in the infinite slab contained between the planes $z=\pm h$, these planes being subject to tractions obtained by reversing the components $\widehat{zz}$ and $\widehat{zr}$ at $z=h$ in I., and $z=-h$ in II.†

Using the notation already given in § 2, the functions χ_1, χ_2, χ_3, representing the systems I., II., and III. respectively, are

$$\left.\begin{aligned} \chi_1 &= \int_0^\infty \frac{\phi_1(k)}{k^3}\left[\{(2\sigma+k(h+z)\}\,J_0(kr)e^{-k(h+z)}\right. \\ &\qquad\qquad \left.-\{2\sigma+(1-2\sigma)k(h+z)\}\right]dk, \\ \chi_2 &= -\int_0^\infty \frac{\phi_1(k)}{k^3}\left[\{2\sigma+k(h-z)\}\,J_0(kr)e^{-k(h-z)}\right. \\ &\qquad\qquad \left.-\{2\sigma+(1-2\sigma)k(h-z)\}\right]dk, \\ \chi_3 &= \int_0^\infty 2\frac{\phi_1(k)}{k^3}\left[(\alpha\sinh kz-\beta kz\cosh kz)\,J_0(kr)\right. \\ &\qquad\qquad \left.-(\alpha-\beta)\,kz\right]dk, \end{aligned}\right\} \quad (47)$$

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* See footnote on preceding page.

† Phil. Mag. *tom. cit.* pp. 1237–1238.

where α and β are given by

$$\left.\begin{aligned} \alpha &= e^{-2hk}\frac{\left[\begin{aligned}&\{2\sigma(1+2hk)+2h^2k^2\}\sinh kh \\ &\qquad + \{hk(1+2hk)-2hk(1-2\sigma)\cosh kh\end{aligned}\right]}{2hk+\sinh 2hk}, \\ \beta &= e^{-2hk}\frac{[(1+2hk)\sinh kh + 2hk\cosh kh]}{2hk+\sinh 2hk}. \end{aligned}\right\} \quad (48)$$

These quantities have been tabulated *, assuming Poisson's Ratio $\sigma = \cdot 3$, and are negligible for values of $hk > 4$.

(b) *Evaluation of Stress-Components and Displacements.*

For the stress-systems I. and II., of the system (A), equations (6) give the stress-components at any point, by writing $(h+z)$ and $(h-z)$ for z respectively. For the system III. the stress-components become

$$\left.\begin{aligned} \widehat{rr}_3 &= -2\int_0^\infty \phi_1(k)\Big[2\beta\sigma\cosh kz\, J_0(kr) - \Big\{J_0(kr) - \frac{J_1(kr)}{kr}\Big\} \\ &\qquad\qquad \times \{(\alpha-\beta)\cosh kz - \beta\, kz\sinh kz\}\Big]\,dk, \\ \widehat{\theta\theta}_3 &= -2\int_0^\infty \phi_1(k)\Big[2\beta\sigma\cosh kz\, J_0(kr) - \frac{J_1(kr)}{kr} \\ &\qquad\qquad \times \{(\alpha-\beta)\cosh kz - \beta\, kz\sinh kz\}\Big]\,dk, \\ \widehat{zz}_3 &= -2\int_0^\infty \phi_1(k)\Big[\{\alpha+\beta(1-2\sigma)\}\cosh kz \\ &\qquad\qquad - \beta\, kz\sinh kz\Big]\, J_0(kr)\,dk. \end{aligned}\right\} \quad . \quad . \quad . \quad (49)$$

The components $\widehat{zr}$ for the three systems are given by

$$\left.\begin{aligned} \widehat{zr}_1 &= \int_0^\infty \phi_1(k)\, e^{-k(h+z)} k(h+z)\, J_1(kr)\,dk, \\ \widehat{zr}_2 &= -\int_0^\infty \phi_1(k)\, e^{-k(h-z)} k(h-z)\, J_1(kr)\,dk, \\ \widehat{zr}_3 &= -2\int_0 \phi_1(k)\,[\beta\, kz\cosh kz - (\alpha-2\beta\sigma)\sinh kz]\, J_1(kr)\,dk. \end{aligned}\right\} \quad . \quad . \quad . \quad (50)$$

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* Phil. Mag. *tom. cit.* p. 1242.

Expressing the coordinates r, z, in terms of h, these integrals may be evaluated graphically, and the stress-components, in every case, written in the form *

$$\widehat{rr} = \delta_{rr} \cdot \frac{P}{\pi h^2}, \qquad \ldots \ldots \ldots \quad (51)$$

where $\delta_{\widehat{rr}} = \delta_{\widehat{rr}_1} + \delta_{\widehat{rr}_2} + \delta_{\widehat{rr}_3}$, and so on,

the numerical constant $\delta_{\widehat{rr}}$ representing the stress-component $\widehat{rr}$ at the point considered.

In a similar manner, the displacements in the systems I. and II., of the stress-system (A), are obtained from equations (8), while for the system III. the displacements are determined from the function χ_3 given by equation (44).

Putting $z=h$, we have, at the plane face of the disk, for the system (A)

$$\left.\begin{aligned}
w_1 &= -\frac{2(1+\sigma)}{E}\int_0^\infty \frac{\phi_1(k)}{k} e^{-2kh}\{(1-\sigma)+kh\}J_0(kr)\,dk,\\
w_2 &= \frac{2(1-\sigma^2)}{E}\int_0^\infty \frac{\phi_1(k)}{k} J_0(kr)\,dk,\\
w_3 &= -\frac{2(1+\sigma)}{E}\int_0^\infty \frac{\phi_1(k)}{k}\big[\{\alpha+2\beta(1-2\sigma)\}\sinh kh\\
&\qquad\qquad -\beta\, kh\cosh kh\big]J_0(kr)\,dk\,;
\end{aligned}\right\} \quad (52)$$

$$\left.\begin{aligned}
u_1 &= \frac{(1+\sigma)}{E}\int_0^\infty \frac{\phi_1(k)}{k} \cdot e^{-2kh}\\
&\qquad\qquad \cdot\{(1-2\sigma)-2kh\}J_1(kr)\,dk,\\
u_2 &= \frac{(1+\sigma)(1-2\sigma)}{E}\int_0^\infty \frac{\phi_1(k)}{k} J_1(kr)\,dk,\\
u_3 &= \frac{2(1+\sigma)}{E}\int_0^\infty \frac{\phi_1(k)}{k}\big[(\alpha-\beta)\cosh kh\\
&\qquad\qquad -\beta\, kh\sinh kh\big]J_1(kr)\,dk.
\end{aligned}\right\} \quad (53)$$

Expressing these displacements in the form

$$\left.\begin{aligned}
w &= \gamma_w \cdot \frac{P}{\pi h E},\\
u &= \gamma_u \cdot \frac{P}{\pi h E},
\end{aligned}\right\} \quad \ldots \ldots \quad (54)$$

where

$$\gamma_w = \gamma_{w_1} + \gamma_{w_2} + \gamma_{w_3},$$
$$\gamma_u = \gamma_{u_1} + \gamma_{u_2} + \gamma_{u_3},$$

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* Phil. Mag. *tom. cit.* p. 1243.

then, when $\phi_1(k)$ is known, the integrations for the systems I. and III. may be performed graphically, and numerical values for γ_w and γ_u obtained.

The strains may be determined directly from the stress-components by writing

$$\lambda\widehat{rr} = \delta\widehat{rr} - \sigma(\delta\widehat{\theta\theta} + \delta\widehat{zz}) \text{ etc.,}$$

λ being a constant representing a particular strain in the system (A), such that

$$e_{rr} = \lambda_{rr} \cdot \frac{\text{P}}{\pi \text{E} h^2}, \text{ etc.} \quad . \quad . \quad . \quad . \quad (55)$$

§ 5. The Stress-System (A) due to a Symmetrical Distribution of Tangential Surface Traction, in a Complete Disk at Rest.

(a) Here the system will be made up of three component systems as in the previous article. The functions χ_1, χ_2, χ_3, representing the systems I., II., and III., respectively, are

$$\left.\begin{aligned}
\chi_1 &= \int_0^\infty \frac{\phi_2(k)}{k^3}\big[\{(1-2\sigma)-k(h+z)\}\,\text{J}_0(kr)\,e^{-k(h+z)} \\
&\qquad\qquad -\{(1-2\sigma)-2k(h+z)(1-\sigma)\}\big]\,dk, \\
\chi_2 &= -\int_0^\infty \frac{\phi_2(k)}{k^3}\big[\{(1-2\sigma)-k(h-z)\}\,\text{J}_0(kr)\,e^{-k(h-z)} \\
&\qquad\qquad -\{(1-2\sigma)-2k(h-z)(1-\sigma)\}\big]\,dk, \\
\chi_3 &= \int_0^\infty \frac{2\phi_2(k)}{k^3}\big[(\alpha\sinh kz-\beta\, kz\cosh kz)\,\text{J}_0(kr) \\
&\qquad\qquad -(\alpha-\beta)\,kz\big]\,dk.
\end{aligned}\right\} \quad (56)$$

The condition for determining the constants α and β is the same as in the previous case. These may be written

$$\left.\begin{aligned}
\alpha &= -e^{-2hk}\,\frac{\begin{bmatrix}\{hk(1+2hk)-2hk(1-2\sigma)\}\sinh kh \\ +\{(1-2\sigma)(1-2hk)+2h^2k^2\}\cosh kh\end{bmatrix}}{2hk+\sinh 2hk}, \\
\beta &= -e^{-2hk}\,\frac{[2hk\sinh kh-(1-2hk)\cosh kh]}{2hk+\sinh 2hk}.
\end{aligned}\right\} \quad (57)$$

Assuming Poisson's Ratio $\sigma = \cdot 3$, calculated values of these constants are given in Table I.

TABLE I.

hk.	*α.*	*β.*
0	$-\infty$	$+\infty$
·25	−·2137	·2305
·50	−·1482	−·0882
·75	−·1380	−·1156
1·0	−·1217	−·0938
1·5	−·0723	−·04235
2·0	−·0328	−·01509
3·0	−·00415	−·00132
4·0	−·00038	−·000092
5·0	−·0000297	−·0000058
6·0	−·00000215	−·00000035

(b) *Evaluation of Stress-Components and Displacements.*

For the stress-systems I. and II., equations (31) give the stress-components at any point, by writing $(h+z)$ and $(h-z)$ for z respectively. For the system III., the corresponding components are given by equations (49), using the values of α and β just determined, and replacing $\phi_1(k)$ by $\phi_2(k)$ in these equations.

The components $\widehat{zr}$ for the three systems are

$$\left.\begin{aligned}\widehat{zr}_1 &= \int_0^\infty \phi_2(k)\, e^{-k(h+z)}\{1-k(h+z)\}\,\mathrm{J}_1(kr)\,dk,\\ \widehat{zr}_2 &= -\int_0^\infty \phi_2(k)\, e^{-k(h-z)}\{1-k(h-z)\}\,\mathrm{J}_1(kr)\,dk,\\ \widehat{zr}_3 &= -2\int_0^\infty \phi_2(k)\,\{\beta kz\cosh kz-(\alpha-2\beta\sigma)\sinh kz\}\,\mathrm{J}_1(kr)\,dk.\end{aligned}\right\} \quad . \quad . \quad . \quad (58)$$

As before, the stress-components at any point may be represented by numerical constants, and written in the form

$$\widehat{rr}=\delta_{\widehat{rr}}\cdot\frac{\mathrm{Q}}{\pi h^2},\ \text{etc.}, \quad . \quad . \quad . \quad . \quad . \quad (59)$$

the constants δ to be determined graphically. The displacements for the systems I. and II. are obtained from equations (33), while for the system III. they are given in equations (52) and (53), using the appropriate values of α and β, and replacing $\phi_1(k)$ by $\phi_2(k)$ in these equations.

When $\phi_2(k)$ is known, the displacements may again be written

$$\left.\begin{aligned} w &= \gamma_w \cdot \frac{Q}{\pi h E} \\ u &= \gamma_u \cdot \frac{Q}{\pi h E} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (60)$$

and numerical values determined as before.

§ 6. THE STRESS-SYSTEM (B).

For reference, the results of the solution due to Chree are summarized below. The stress-components are given by

$$\left.\begin{aligned} rr &= \frac{\rho\omega^2}{8}(3+\sigma)(a^2-r^2) + \frac{\rho\omega^2}{6}\sigma\frac{(1+\sigma)}{(1-\sigma)}(h^2-3z^2), \\ \widehat{\theta\theta} &= \frac{\rho\omega^2}{8}\{(3+\sigma)a^2-(1+3\sigma)r^2\} + \frac{\rho\omega^2}{6}\sigma\frac{(1+\sigma)}{(1-\sigma)}\cdot(h^2-3z^2), \\ \widehat{zz} &= \widehat{zr} = 0, \end{aligned}\right\} \quad . \quad . \quad . \qquad (61)^*$$

and the displacements by

$$\left.\begin{aligned} u &= \frac{\rho\omega^2 r}{8E}(1-\sigma)\{(3+\sigma)a^2-(1+\sigma)r^2\} \\ &\qquad + \frac{\rho\omega^2}{6E}\cdot r\sigma(1+\sigma)(h^2-3z^2), \\ w &= -\frac{\rho\omega^2 z}{4E}\sigma\{(3+\sigma)a^2-2(1+\sigma)r^2\} \\ &\qquad - \frac{\rho\omega^2}{3E}\cdot z\cdot\sigma^2\frac{(1+\sigma)}{(1-\sigma)}(h^2-z^2). \end{aligned}\right\} \qquad (62)$$

§ 7. CALCULATED VALUES OF THE STRESS-COMPONENTS AND DISPLACEMENTS IN THE SYSTEM (A). DETERMINATION OF P AND Q.

For any assumed distribution of traction the functions $\phi_1(k)$ and $\phi_2(k)$ may be determined, and the stress-components for the system (A) calculated in terms of P and Q, the total normal and tangential loads applied to the plane faces of the disk at rest. It remains to calculate these quantities P and Q in terms of ω. Three cases are considered.

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* ρ being the density in these equations.

Case 1.—*Disk restrained by a Distribution of Normal Traction only.*

Here Q is zero. For the determination of P in terms of ω we may suppose that, for the systems (A) and (B) combined,

(i.) The resultant axial displacement vanishes at $z = \pm h$, $r = 0$, or

(ii.) The resultant axial strain vanishes at $z = 0$, $r = 0$.

Table II.

$\phi_1(k) = \frac{Pk}{2\pi} J_0\left(\frac{hk}{4}\right)$.	Plane $z=0$.			Plane $z=\frac{h}{2}$.			Plane $z=h$.	
	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.
$r=0$ ……	−·234	−·234	2·171	−·072	−·072	3·64	− ·475	−·475
$r=\frac{h}{4}$ ……	−·135	−·226	1·899	·058	−·136	3·036	− ·442 −3·642	−·455 2·745
$r=\frac{h}{2}$ ……	·074	−·191	1·283	·424	−·162	1·391	−1·167	·392
$r=\frac{3h}{4}$ ……	·224	−·153	·695	·413	−·135	·470	− ·625	·008
$r=h$ ……	·255	−·115	·296	·257	−·103	·154	− ·372	−·085
$r=\frac{5h}{4}$ ……	·218	−·086	·106	·150	−·084	·048	− ·220	−·099
$r=\frac{3h}{2}$ ……	·164	−·066	·020	·088	−·068	·010	− ·122	−·084
$r=\frac{7h}{4}$ ……	·114	−·052	−·010	·058	−·054	−·007	− ·057	−·062
$r=2h$ ……	·075	−·043	−·019	·042	−·044	−·011	− ·019	−·043

Subcase (a).—*P round a Circumference of Radius* b: § 2 *b*.

$$\phi_1(k) = \frac{Pk}{2\pi} J_0(kb).$$

Values of δ, representing the total stress-components in the system (A), when $b = \frac{h}{4}$, $\frac{h}{2}$, $\frac{3h}{4}$, and h, are shown in Tables II. to V. respectively *. The surface displacements w, corresponding to these distributions, may be obtained from Table VI.

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* Calculated values for the case when $b=0$ have already been tabulated. Phil. Mag. *tom. cit.* Table III. p. 1244, and figs. 1, 2, and 3.

TABLE III.

$\dfrac{\phi_1(k)}{\frac{Pk}{2\pi}J_0\frac{(hk)}{2}}$.	Plane $z=0$.			Plane $z=\frac{h}{2}$.			Plane $z=h$.	
	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.
$r=0$ ……	−·056	−·056	1·348	−·206	−·206	1·201	−·401	−·401
$r=\frac{h}{4}$ ……	−·051	−·066	1·283	·090	·172	1·391	−·383	−·390
$r=\frac{h}{2}$ ……	·005	−·080	1·072	·007	·065	1·45	−·334 −1·134	−·363 ·437
$r=\frac{3h}{4}$ ……	·098	−·086	·726	·202	−·035	·770	−·615	·038
$r=h$ ……	·172	−·081	·384	·233	−·073	·280	−·377	−·068
$r=\frac{5h}{4}$ ……	·180	−·070	·166	·161	−·072	·085	−·236	−·088
$r=\frac{3h}{2}$ ……	·149	−·058	·050	·102	−·063	·024	−·137	−·080
$r=\frac{7h}{4}$ ……	·110	−·047	·004	·065	−·052	·002	−·071	−·063
$r=2h$ ……	·074	−·041	−·011	·046	−·043	−·007	−·028	−·046

TABLE IV.

$\dfrac{\phi_2(k)}{\frac{Pk}{2\pi}J_0\frac{(3hk)}{4}}$.	Plane $z=0$.			Plane $z=\frac{h}{2}$.			Plane $z=h$.	
	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.
$r=0$ ……	·051	·051	·668	·146	·146	·381	−·317	−·317
$r=\frac{h}{4}$ ……	·030	·042	·695	·127	·151	·470	−·306	−·311
$r=\frac{h}{2}$ ……	−·008	·022	·726	·019	·148	·770	−·281	−·298
$r=\frac{3h}{4}$ ……	−·003	−·005	·670	−·055	·094	·93	−·235 −·591	−·272 ·084
$r=h$ ……	·057	−·029	·470	·105	−·001	·498	−·378	−·036
$r=\frac{5h}{4}$ ……	·110	−·043	·260	·156	−·043	·184	−·251	−·071
$r=\frac{3h}{2}$ ……	·122	−·044	·116	·114	−·051	·061	−·159	−·070
$r=\frac{7h}{4}$ ……	·107	−·042	·040	·074	−·049	·017	−·094	−·061
$r=2h$ ……	·081	−·037	·003	·048	−·043	·002	−·048	−·050

TABLE V.

$\phi_1(k)$ $\frac{Pk}{2\pi}J_0(hk)$.	Plane $z=0$.			Plane $z=\frac{h}{2}$.			Plane $z=h$.	
	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.
$r=0$	·08	·08	·271	·072	·072	·122	−·232	−·232
$r=\frac{h}{4}$	·063	·078	·296	·075	·079	·154	−·228	−·230
$r=\frac{h}{2}$	·022	·071	·384	·066	·094	·280	−·219	−·224
$r=\frac{3h}{4}$	−·023	·052	·470	−·009	·113	·498	−·199	−·211
$r=h$	−·025	·020	·473	−·072	·085	·709	−·172 −·372	−·196 ·004
$r=\frac{5h}{4}$	·019	−·006	·352	·056	·017	·384	−·280	−·047
$r=\frac{3h}{2}$	·066	−·022	·200	·105	−·024	·148	−·188	−·060
$r=\frac{7h}{4}$	·087	−·029	·087	·083	−·035	·046	−·118	−·055
$r=2h$	·079	−·033	·025	·052	−·032	·013	−·070	−·049

TABLE VI.

	$b=0$.		$b=\frac{h}{4}$.		$b=\frac{h}{2}$.		$b=\frac{3h}{4}$.		$b=h$.	
	$\gamma_{w_{1+3}}$.	γ_{w_2}.	$\gamma_{w_{1+3}}$.	γ_{w_2}.	$\gamma_{w_{1+3}}$.	γ_{w_2}.	$\gamma_{w_{1+3}}$.	γ_{w_2}.	$\gamma_{w_{1+3}}$.	γ_{w_2}.
$=0$	−1·059	—	−1·042	3·64	−·982	1·82	−·896	1·213	−·796	·91
$=\frac{h}{4}$	−1·042	3·64	−1·021	—	−·965	1·955	−·885	1·25	−·790	·928
$=\frac{h}{2}$	−·982	1·82	−·965	1·955	−·920	—	−·854	1·4	−·771	·978
$=\frac{3h}{4}$	−·896	1·213	−·885	1·25	−·854	1·4	−·803	—	−·740	1·104
$=h$	−·796	·91	−·790	·928	−·771	·978	−·740	1·104	−·699	—

In this table the values of γ_{w_2}, for the component-system II. of the stress-system (A), are shown separately.

If $w=0$ at $z=\pm h$, $r=0$, condition (i.) above, then from equation (62), if $\sigma=\cdot 3$, we must have

$$\frac{P}{\pi h^2}=\cdot 2475\frac{\rho\omega^2 a^2}{\gamma_w}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

γ_w representing the total displacement w at $z=h$, $r=0$, for the stress-system (A), and for a particular value of b is found from Table VI.

Alternatively, if $\frac{\partial w}{\partial z}=0$, at $z=0$, $r=0$, $r=0$, condition (ii.) above, then for P we find

$$\frac{P}{\pi h^2}=\frac{\rho\omega^2 a^2}{\lambda_{zz}}\left\{\cdot 2475+\cdot 0557\frac{h^2}{a^2}\right\}. \quad . \quad . \quad . \quad (64)$$

Values of λ_{zz} can be deduced from the stress-components given in Tables II. to V., by means of equation (55). A comparison of these two conditions is shown in Table VII.

TABLE VII.

b/h.	γ_w.	λ_{zz}.
0	—	2·783
$\frac{1}{4}$	2·598	2·311
$\frac{1}{2}$	·833	1·382
$\frac{3}{4}$	·317	·637
1	·114	·223

Subcase (b).—*Where $f(\rho)$ is the given Surface Value of $\widehat{zz}$.*

This is the general case indicated in equation (11). The stress-components and displacements at any point in the system (A) can be found by direct integration from the results of subcase (a), by writing

$$\left.\begin{aligned}\delta' &= \frac{2\pi}{P}\int_0^b \delta f(\rho)\,.\,\rho\,.\,d\rho,\\ \gamma' &= \frac{2\pi}{P}\int_0^b \gamma f(\rho)\,.\,\rho\,.\,d\rho,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (65)$$

the integrations to be performed graphically *.

To illustrate the effect of varying distributions of normal traction on the surface displacements, a distribution varying as ρ^{n-1}, § 2 c, has been chosen. The components of displacement, for the systems I. and III. of the stress-system

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* Where $f(\rho)$ is such that equation (11) may be easily integrated, the stress-components and displacements are determined as outlined in § 4.

(A), have been calculated by means of equations (65) *, and those for the system II. from the results of § 2 *c*.

Table VIII. shows the total displacements in the stress-system (A), at $r=0$ and $r=b$, for varying values of b and n.

TABLE VIII.

	$b=\frac{h}{2}$.			$b=\frac{3h}{4}$.			$b=h$.		
	$r=0$.	$r=b$.		$r=0$.	$r=b$.		$r=0$	$r=b$.	
	γ_w.	γ_w.	γ_u.	γ_w.	γ_w.	γ_u.	γ_w.	γ_w.	γ_u.
$n=1$......	2·618	1·367	·376	1·452	·695	·169	·902	·398	·070
$n=3$......	1·416	1·633	·380	·669	·881	·179	·340	·554	·085
$n=5$......	1·180	1·815	·382	·522	1·005	·183	·240	·651	·094
$n=7$.....	1·081	1·952	·383	·461	1·099	·185	·201	·723	·099
$n=9$......	1·026	2·061	·384	·426	1·174	·187	·181	·780	·101
$n=11$......	·990	2·156	·385	·404	1·238	·188	·167	·829	·103
$n=21$......	·918	2·475	·386	·355	1·453	·191	·138	·993	·108
$n=31$......	·892	2·670	·387	·337	1·584	·192	·128	1·092	·109

Subcase (c).—*Uniform Distribution of Normal Traction* : § 2 *d*.

$$\phi_1(k)=\frac{\mathrm{P}}{\pi b}\mathrm{J}_1(kb)$$

Values of δ representing the total stress-components in the system (A), for the case when $b=h$, are shown in Table IX. If the conditions (i.) and (ii.) are to be satisfied, the corresponding values of P are given by equations (63) and (64), the appropriate values of γ_w and λ_{zz} being ·902 and ·972 respectively

Case 2.—*Disk restrained by a Distribution of Tangential Traction only.*

Here P is zero. For the determination of Q in terms of ω it may be assumed that the resultant radial displacement vanishes at $z=\pm h$, $r=b$.

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* Table VI. is arranged to facilitate these calculations.

TABLE IX.

$\phi_1(k)$ $\frac{P}{\pi h}J_1(hk)$.	Plane $z=0$.			Plane $z=\frac{h}{2}$.			Plane $z=h$.		
	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.
$r=0$	−·010	−·010	·966	·107	·107	1·018	·457	·457	1
$r=\frac{h}{4}$	−·006	−·015	·927	·101	·095	·999	·472	·466	1
$r=\frac{h}{2}$	·013	−·022	·820	·092	·074	·905	·506	·485	1
$r=\frac{3h}{4}$	·048	−·034	·650	·074	·038	·755	·561	·518	1
$r=h$	·096	−·044	·427	·122	−·016	·440	·624 −·376	·557 −·043	1 0
$r=\frac{5h}{4}$	·125	−·049	·234	·139	−·045	·178	−·248	−·075	0
$r=\frac{3h}{2}$	·124	−·046	·103	·106	−·051	·061	−·154	−·072	0
$r=\frac{7h}{4}$	·105	−·042	·034	·071	−·048	·015	−·088	−·061	0
$r=2h$	·079	−·038	·001	·047	−·041	·000	−·044	−·048	0

TABLE X.

$\phi_2(k)$ $\frac{3Q}{2\pi h}J_2(hk)$.	Plane $z=0$.		
	$\widehat{rr}$.	$\widehat{\theta\theta}$.	$\widehat{zz}$.
$r=0$	−·116	−·116	−·595
$r=\frac{h}{4}$	−·121	−·111	−·540
$r=\frac{h}{2}$	−·137	−·091	−·385
$r=\frac{3h}{4}$	−·153	−·071	−·200
$r=h$	−·146	−·052	−·017
$r=\frac{5h}{4}$	−·110	−·043	·082
$r=\frac{3h}{2}$	−·065	−·036	·082
$r=\frac{7h}{4}$	−·030	−·030	·061
$r=2h$	·000	−·026	·040
$r=3h$	—	—	−·002

Taking the distribution given in § 3 *c*, viz., that in which the surface traction varies as the radius, we have

$$\phi_2(k) = \frac{3Q}{2\pi b} J_2(kb).$$

Values of δ representing the stress-components in the system (A), when $b=h$, for the plane $z=0$, are shown in Table X.

If $u=0$ at $z=\pm h$, $r=h$, then from equation (62) it follows that,

$$\frac{Q}{\pi h^2} = -\frac{\rho\omega^2 a^2}{\gamma_u}\left\{\cdot 28875 - \cdot 24375\frac{h^2}{a^2}\right\}, \quad . \quad (66)$$

where $\gamma_u = -\cdot 536.$

Case 3.—*Disk restrained by a Combined Distribution of Normal and Tangential Traction.*

For any assumed distributions two conditions of restraint may be simultaneously satisfied. Take, for example, distributions mentioned in cases 1 and 2, viz.:

$$\phi_1(k) = \frac{P}{\pi b} J_1(kb). \qquad \S\ 2\,d,$$

$$\phi_2(k) = \frac{3Q}{2\pi b} J_2(kb). \qquad \S\ 3\,c.$$

When $b=h$, the surface displacements, at $r=0$ and $r=h$ for the system (A), are contained in Table XI.

TABLE XI.

	$z=h,\ r=0.$	$z=h,\ r=h.$		$z=0,\ r=0.$
	γ_w.	γ_w.	γ_u.	λ_{zz}.
$\phi_1(k)$	·902	·398	·070	·972
$\phi_2(k)$	−·187	·114	−·536	−·526

If, therefore, $w=0$ at $z=\pm h$, $r=0$, and $u=0$ at $z=\pm h$, $r=b$, we have from equation (61)

$$\cdot 902\frac{P}{\pi h E} - \cdot 187\frac{Q}{\pi h E} = \cdot 2475\frac{\rho\omega^2 a^2}{E}\,.\,h,$$

$$\cdot 07\ \frac{P}{\pi h E} - \cdot 536\frac{Q}{\pi h E} = \frac{\rho\omega^2 h}{E}\{\cdot 28875\,a^2 - \cdot 24375\,h^2\},$$

or

$$\left.\begin{aligned}\frac{\mathrm{P}}{\pi h^2}&=\rho\omega^2a^2\left\{\cdot397-\cdot097\frac{h^2}{a^2}\right\},\\ \frac{\mathrm{Q}}{\pi h^2}&=\rho\omega^2a^2\left\{\cdot588-\cdot468\frac{h^2}{a^2}\right\}.\end{aligned}\right\} \quad . \quad . \quad . \quad (67)$$

With these values it follows that

$$\cdot398\frac{\mathrm{P}}{\pi h\mathrm{E}}+\cdot114\frac{\mathrm{Q}}{\pi h\mathrm{E}}=\frac{\rho\omega^2a^2h}{\mathrm{E}}\left\{\cdot225-\cdot092\frac{h^2}{a^2}\right\}.$$

If the condition $w=0$, at $z=\pm h$, $r=b$, were satisfied also, then from equations (61) this displacement should be given by

$$\frac{\rho\omega^2a^2h}{\mathrm{E}}\left\{\cdot2475-\cdot195\frac{h^2}{a^2}\right\}.$$

The condition of complete restraint at the surface of the disk is therefore approximately realized by these assumed distributions of traction.

The total stress-components in the system (A), corresponding to these distributions, may be evaluated by combining the results of Tables IX. and X., using the appropriate values P and Q given by equations (67).

§ 8. SUMMARY AND CONCLUSIONS.

The stresses due to restraint have been taken as those produced in the disk by symmetrical distributions of surface traction, acting on the outside faces of the complete disk at rest, viz., the stress-system (A). The surface displacements arising from these distributions are assumed to neutralize those occurring in a disk rotating under no superficial tractions, viz., the stress-system (B). The total stress-components when rotating under restraint are obtained by combining these two systems.

1. *Disk restrained by Uniform Distributions of Normal Traction.* § 7; Case 1; Subcase (c).

For the stress-system (A) we can now write stress-component $=\delta\cdot\frac{\mathrm{P}}{\pi h^2}=\cdot2475\cdot\frac{\delta}{\gamma_r}\cdot\rho\omega^2a^2$, where $\gamma_w=\cdot902$, satisfies the condition $w=0$, $z=\pm h$, $r=0$. Values of δ are shown in Table IX. It will be noted that a discontinuous change occurs in these stress-components at the circumference $r=h$, $z=h$. The maximum values occurring at this point when $r<h$, are as follows :—

$$\left.\begin{aligned} \widehat{rr} &= \cdot 693\,\rho\omega^2 a^2, \\ \widehat{\theta\theta} &= \cdot 618\,\rho\omega^2 a^2, \\ \widehat{zz} &= 1\cdot 109\,\rho\omega^2 a^2. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (68)$$

For the stress-system (B), when $r=h$, $z=h$, equations (61) give

$$\left.\begin{aligned} \widehat{rr} &= \rho\omega^2 a^2 \left\{ \cdot 4125 - \cdot 598\,\frac{h^2}{a^2} \right\}, \\ \widehat{\theta\theta} &= \rho\omega^2 a^2 \left\{ \cdot 4125 - \cdot 423\,\frac{h^2}{a^2} \right\}; \\ \widehat{zz} &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad (69)$$

From Table VIII., when $n=1$, it will be noticed that γ_w, at $r=h$, is ·398. Comparing this with the value ·902, at $r=0$, it follows that the distribution of normal traction which will produce plane strain over the circular area of radius h must give rise to a greater stress-concentration at the point of discontinuity than is indicated by equations (68). It is probable, however, that the stresses fall more or less rapidly at this point whatever the assumed distribution of normal traction may be.

2. *Disk restrained by a Distribution of Tangential Traction varying at the Radius.* § 7 ; Case 2.

This is of interest, in that the resultant axial pull is everywhere zero. For the stress-system (A) we have, as before,

stress-component=

$$\delta . \frac{Q}{\pi h^2} = -\rho\omega^2 a^2 . \frac{\delta}{\gamma_u} \left\{ \cdot 28875 - \cdot 24375\,\frac{h^2}{a^2} \right\},$$

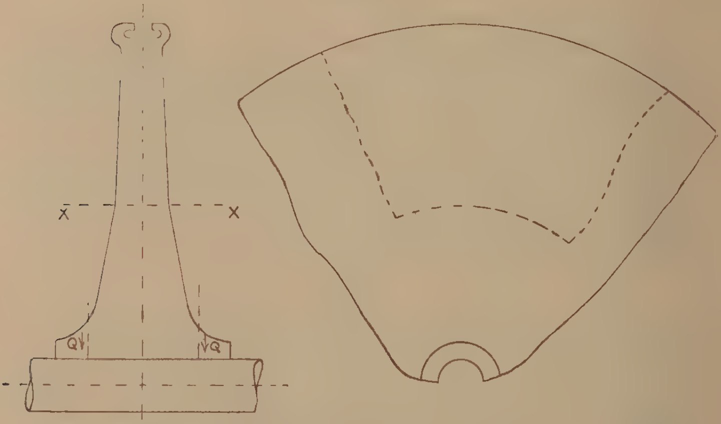
where $\gamma_u = -\cdot 536$ satisfies the condition $u=0$ at $z=\pm h$, $r=h$. Values of δ. for the plane $z=0$, are shown in Table X. An examination of equations (31) shows that the stress-components, $\widehat{rr}$ and $\widehat{\theta\theta}$, at the circumference $r=h$, $z=h$, are infinite. It will be noted also that on the plane $z=0$ the component $\widehat{zz}$ changes sign at $r=h$ very nearly, so that in a disk carried on a shaft which can withstand no axial pull, radial restraint renders the shaft in a state of compression.

3. *Disk restrained by the Combined Distributions of Normal and Tangential Traction:* § 7 ; Case 3.

For the system (A) the stress-components may be determined from Tables IX. and X., using the appropriate values of P and Q, equations (67). As already mentioned, a uniform distribution of normal traction, combined with a distribution of tangential surface traction varying as the radius, produces an approximate condition of complete restraint over the region of the applied loads.

In conclusion it is interesting to note that radial restraint can only be realized by the application of tangential surface tractions acting on the plane faces of the disk.

Fig. 2.



For the purely theoretical case, dealt with in the foregoing analysis, the abrupt change of section at the junction of the disk and the shaft give rises to stress-concentration at this point. In practice, changes of section, although not so abrupt, will produce the same effect. A turbine disk of profile somewhat as shown in fig. 2, having an abrupt change of angle at the section XX, fractured by two opposite pieces flying out.

The nature of the stresses produced might be inferred from the assumption that the central portion is restrained by tangential tractions Q, when, considering the problem from the point of view of case (2) above, it can be seen that the axial component of stress $\widehat{zz}$ will reach its maximum tensile value somewhere in the region XX of the disk.

CIV. *On the Variation with Temperature of Thermal Separation in Gaseous Mixtures.* *By* J. W. H. LUGG, *B.Sc., University of Western Australia* [*].

Introduction.

IN their development of the kinetic theory of gases, Enskog and Chapman[†] have shown that the existence of a temperature gradient in a binary gas mixture will in general result in a process of thermal diffusion whereby a composition gradient will ultimately be established. This prediction was verified experimentally by Chapman and Dootson[‡], and the phenomenon has been further studied by Ibbs[§] and by Elliott and Masson[||].

Chapman has also shown, by means of calculations based on the use of certain simplified molecular models, that in equilibrium the composition gradient should be proportional to the gradient of the logarithm of the absolute temperature, the proportionality factor, k_T, being a complex function of the composition of the mixture. For a small composition difference, $\Delta\lambda$, an approximate integration is readily effected, and gives the expression :—

$$\Delta\lambda = k_T \ln \frac{T_2}{T_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\Delta\lambda$ is the (small) composition difference between two portions of the mixture whose absolute temperatures are T_1 and T_2 respectively, and k_T is independent of temperature ; ln denotes the Napierian logarithm.

Ibbs[¶] verified this conclusion by experiments in which the cold portion was at room temperature whilst the temperature of the hot portion was varied between room temperature and 230° C. Nevertheless, Elliott and Masson[**] obtained values of k_T for H_2-CO_2 and for $He-CO_2$ mixtures, when the two temperatures were

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[*] Communicated by Prof. S. Chapman, F.R.S.

[†] D. Enskog, *Phys. Zeit.* xii. p. 538 (1911) ; *Ann. d. Phys.* xxxviii. p. 742 (1912). S. Chapman, Phil. Trans. ccxvi. A, p. 279 (1915), and ccxvii. A, p. 115 (1916).

[‡] Phil. Mag. xxxiii. p. 249 (1917).

[§] Proc. Roy. Soc. xcix. A, p. 385 (1921), cvii. A, p. 470 (1925), etc.

[||] *Ibid.* cviii. A, p. 378 (1925).

[¶] *Ibid.* xcix. A, p. 385 (1921) ; cvii. A, p. 470 (1925), etc.

[**] *Ibid.* cviii. A, p. 378 (1925).

0° C. and 490° C. respectively, which were considerably greater than Ibbs' corresponding values.

These results suggest that the logarithmic formula may not always be valid at high temperatures, and the present investigation was undertaken with the object of further exploring the region between 230° C. and 490° C., in order to determine whether the observed variation of k_T could be confirmed, and, in the event of it being confirmed, to study the conditions under which the logarithmic formula becomes invalid *.

Experimental.

The arrangement of the diffusion bulbs and the methods of manipulation of the gases were similar to those adopted by Elliott and Masson †.

All the experiments (except one) were carried out with a mixture of hydrogen and carbon dioxide of constant composition. Hydrogen was prepared electrolytically and purified by passage through a silica tube containing metallic copper maintained at a dull red heat. It was finally dried by being slowly led over phosphorus pentoxide. The carbon dioxide was similarly led over phosphorus pentoxide. The carbon dioxide was similarly dried, and it was subsequently tested for purity by absorption with caustic potash; the unabsorbed residue was quite negligible in amount.

The gas mixture was stored in bulk over mercury, and samples were drawn off through a capillary siphon as required. The differences in viscosity between hydrogen and carbon dioxide effected a variation in the composition of the sample which was not greater than ·001 or ·002 in the fraction of a constituent. Manipulation measures were taken to prevent cumulative variation in composition of the supply of mixture.

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* Note by S. Chapman.—Since Mr. Lugg first sent me the results here communicated, a paper by T. L. Ibbs, K. E. Grew, and A. A. Hirst has appeared (Proc. Phys. Soc. xli. p. 456, Aug. 1929) in which experiments on thermal diffusion at *low* temperatures are described. They find that as the temperature of liquefaction of one of the constituent gases in their mixtures is approached, k_T decreases. This is in general agreement with Mr. Lugg's result for the H_2—CO_2 mixture (in which one constituent (CO_2) is easily liquefied), that k_T increases at high temperatures; his explanation also is similar to that given by Dr. Ibbs and his collaborators. Mr. C. T. L. Caton is investigating the theoretical variation of k_T, taking account of attractive as well as repulsive forces.

† Proc. Roy. Soc. cviii. A, p. 378 (1925).

Temperature Control and Measurement.

The temperature of the cold bulb was maintained constant at 29° C. or approximately 302° A. The hot-bulb temperature was varied between 100°C. and 470° C.

For most of the diffusions the cold bulb was jacketed in cotton-wool with an accurate thermometer against the side of the bulb. A stone jar which could be gently heated if the room temperature were to fall below 29° C. surrounded this arrangement. Later it was found that a water-jacket for the cold bulb afforded somewhat better temperature control. A water-jacket was therefore employed in the last few diffusions.

Steam at 100° C. was employed to heat the hot bulb for one diffusion. In all other cases an electric furnace, wired and otherwise adjusted so as to eliminate end effects almost completely, was used. A mercury thermometer, nitrogen filled and reading to 560° C., was supported against the bulb in the furnace. The thermometer was carefully calibrated, and the temperature of the hot bulb at any moment could be determined to within a degree or two over the entire range of temperature employed.

In many instances the diffusion was allowed to take place overnight, but variations in the voltage of the mains necessitated completion of each diffusion the following day, with continual observation and adjustment of furnace rheostats so as to maintain the furnace at one temperature for five hours or more. A few of the earlier results were vitiated by failure to observe this precaution, and these are not included in this communication.

Analysis of Contents of the Diffusion Bulbs.

A direct method was employed. A volume of the mixture was measured, and remeasured after absorption of the carbon dioxide. Although in the first cases two samples of each mixture were analysed, it was soon realised that the total volumes from the bulbs would have to be analysed if good accuracy were to be attained.

Correction for Gas contained in Connecting Tubing.

The presence of gas in the small tubing connecting the hot and cold diffusion bulbs necessitated the application of a correction to the observed compositions. It was considered justifiable to assume that for both hot and cold bulbs this tubing was at the temperature of the cold bulb, viz., 29° C. On this basis a correction was necessary only in the case of the hot-bulb composition.

Results.

The experimental results are summarised in Table I. Here T_1 and T_2 represent the absolute temperatures and λ_1 and λ_2 the compositions, expressed in fractions of hydrogen, of the cold and hot bulbs respectively. Column (7) contains the values for the composition of the hot bulbs obtained after correcting for the amount of cold gas present in the connecting tubes, whilst in column (8) values of the corrected composition difference, $\Delta\lambda$, are given. λ represents the composition of the gas mixture before diffusion.

Table I.

Vol. of cold bulb ... 27·451 mils. Vol. of hot bulb... 50·362 mils.
Vol. of leads... ... 1·393 mils. Vol. of leads ... 1·526 mils.

(1) No.	(2) T_1	(3) T_2	(4)	(5) 1	(6) 2	(7) 2 (corr.)	(8) (7)–(5)
1	299	676	0·50890	0·47876	0·54467	0·54919	0·07043
2	302	373·2	·53215	·52200	·53671	·53725	·01525
3	„	477·3	„	·51568	·54708	·54855	·03287
4	„	486·7	„	·51382	·54738	·54893	·03511
5	„	486·7	„	·51374	·54742	·54899	·03527
6	„	531·2	„	·50835	·55231	·55465	·04630
7	„	582·7	„	·50489	·55653	·55945	·05456
8	„	628·7	„	·50177	·56171	·56549	·06372
9	„	680·5	„	·49967	·56721	·57184	·07217
10	„	736·8	„	·49807	·57320	·97850	·08047
11	„	—	„	—	—	—	—

The first diffusion does not belong to the series 2–11. In diffusion No. 11 the temperature of the hot bulb was in the neighbourhood of 520° C. and the glass gave way, being a softer variety than was anticipated. There is reason to believe that in diffusion No. 10 the amount of separation may be too low in value, since the furnace temperature was rather low overnight.

The total gas pressure during diffusion lay between the limits 0·5 to 1 atmosphere. The fourth and fifth diffusions indicate that the composition difference is most probably independent of the total pressure within these limits. For these two experiments the ratio of the pressures during diffusion was 1·61, other variables being unchanged; the thermal separations, however, were almost identical.

Discussion.

These results have been used to calculate the values of k_T, the "constant" in Chapman's integrated logarithmic formula (Equation (1) above) and also a quantity K defined by the identity $K = \Delta\lambda/(T_2 - T_1)$. The values of these quantities are given in Table II.

TABLE II.

No.	T_2.	k_T.		K.
2	373·2	0·07204	...	$0{\cdot}0_3 2142$
3–	477·3	·07181	...	${\cdot}0_3 1875$
4 and 5	486·7	·07356	...	${\cdot}0_3 1901$
6	531·2	·08218	...	${\cdot}0_3 2020$
7	582·7	·08302	...	${\cdot}0_3 1944$
8	628·7	·08690	...	${\cdot}0_3 1950$
9	680·5	·08844	...	${\cdot}0_3 1907$
10	736·8	·09023	...	${\cdot}0_3 1851$
			Mean ...	${\cdot}0_3 195$

The gradual increase of k_T as the temperature T_2 of the hot bulb is raised is unmistakable. It must, however, be borne in mind that, since k_T depends on the composition of the mixture, equation (1) is not strictly applicable, especially at the higher temperature where $\Delta\lambda$ is large. To minimise complications of this nature the composition of the initial mixture was chosen so that for small separations k_T should be near its maximum value, as determined by Ibbs. For this composition the fact that the separation is large will not greatly affect the validity of the present calculations of k_T; moreover, any small error which might be introduced in this way should result in an apparent decrease of k_T at the higher temperatures. The use of the integrated equation therefore certainly does not diminish the qualitative significance of the results in Table II.

At low temperatures the results check approximately with those of Ibbs for a similar gas-mixture, viz., $k_T = 0{\cdot}070$, but at higher temperatures K is more nearly a constant than k_T. It may perhaps be noted that over the temperature range used by Ibbs (room temperature to 230° C.) the linear and logarithmic relationships would be difficult to distinguish experimentally.

Using the mean value of K ($\cdot 0_3 195$), $\Delta\lambda$ for a temperature difference of 486° A. would have the value 0·0948. Using the same temperature difference, Elliott and Masson obtained the value 0·1034 for a mixture giving the *maximum* separation.

The theoretical significance of the observed increase of k_T with temperature will not be discussed here, though it may perhaps be pointed out that such an increase might be expected if the character of the intermolecular collisions approximated more closely at the higher temperatures to that of collisions between perfectly elastic spheres.

Summary.

1. The thermal separations for a single mixture of hydrogen and carbon dioxide have been studied with the cold-bulb temperature at 29° C. and the hot bulb at temperatures between 100° C. and 464° C.

2. The results indicate that the separations at the higher temperatures are greater than would be expected on the basis of Chapman's logarithmic formula. The relationship between composition difference and temperature difference is more nearly linear.

In conclusion, the author desires to acknowledge his indebtedness to the founders of the Amy Saw Scholarship and to the Government of Western Australia for pecuniary assistance, and to Dr. G. A. Elliott for suggesting this research and for his advice and instruction during its progress. Thanks are also due to Professor N. T. M. Wilsmore for his advice and for the provision of laboratory facilities, and to Professor S. Chapman for his interest and assistance in publication.

Sept. 23, 1929.

CV. *On the Multiplication of Serial Relations.* By D. M. Wrinch, *M.A., D.Sc., Lecturer at Lady Margaret Hall, Oxford* [†].

In this paper we give the relations between the element and gap characters of any series, P and Q, and the series Q × P obtained by multiplying the two series together.

It will be assumed that a term cannot be the sequent of an ω_m and an ω_n unless $m=n$.

Let ν_1, μ_1 and ν_2, μ_2 be any element character of P and Q respectively, where $\nu_1 \neq \varpi$, $\mu_1 \neq \varpi$, $\nu_2 \neq \varpi$, $\mu_2 \neq \varpi$. And let σ_1, ρ_1 and σ_2, ρ_2 be any gap character of P and Q respectively, where $\sigma_1 \neq \varpi$, $\sigma_2 \neq \varpi$, $\rho_1 \neq \varpi$, $\rho_2 \neq \varpi$. Further, let n_1, ϖ ; ϖ, m_1, and n_2, ϖ; ϖ, m_2 be characters of P and Q respectively [‡]. If P has a beginning, n_1, ϖ will be an element character, otherwise it will be a gap character; if P has an end, ϖ, m_1 will be an element character, otherwise it will be a gap character. In the same way, if Q has a beginning, n_2, ϖ will be an element character, otherwise it will be a gap character; if Q has an end, ϖ, m_2 will be an element character, otherwise it will be a gap character. It is assumed that ν's, μ's, n's, and m's only have inductive numbers or 0 or -1 as values.

§ 1. The members of the field of P × Q will be in the form of a couple xy, where x is a member of the field of P, and y is a member of the field of Q [||]. Since P and Q are series, so also is Q × P [¶]. A couple x_1y_1 precedes a couple x_2y_2 in the Q × P order, if $y_1 \mathrm{Q} y_2$ whatever the relation of x_1 to x_2, or if $y_1 = y_2$ and $x_1 \mathrm{P} x_2$. There will therefore be stretches of the series Q × P in which the Q-term remains constant and the P-term runs through the whole of the P-series. Such a stretch is ordinally similar to P. Hence ν_1, μ_1 will be an element character of the stretch. If $n_1, \varpi \,\epsilon\,$ elt‘P, this stretch will have a first term which is an ${}^*\omega_n$-predecessor; if $n_1, \varpi \,\epsilon\,$ gap‘P, this stretch will be coinitial with an ${}^*\omega_{n_1}$. If $\varpi_1, m_1 \,\epsilon\,$ elt‘P, it will have a last term which is an ω_{m_1}-sequent; and if $\varpi, m_1 \,\epsilon\,$ gap‘P, it will have an ω_{m_1}-

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[†] Communicated by the Author.

[‡] We systematize a term which is the last term of a series, as a ϖ, m_1 element, and a term which is the first term of a series as a n_1, ϖ element.

[||] See ‘Principia Mathematica,’ *166.

[¶] *Op. cit.* *204.55.

confinal with it. Suppose y, the Q-term, has the character ν_2, μ_2. Let

$$r_1 r_2 \ldots r_\zeta \ldots \qquad \zeta < \omega_{\mu_2}$$

be a series contained in Q, having y as its sequent. If $\mu_2 \neq -1$, if $n_1, \varpi \epsilon \text{elt}`\text{P}$, and x_0 is the first term of P, $x_0 y$ is the sequent of the series

$$xr_1, xr_2, \ldots xr_\zeta \ldots \qquad \zeta < \omega_{\mu_2},$$

where x is any P-term; and this series is an ω_{μ_2} contained in $\text{Q} \times \text{P}$. Consequently, if $\mu_2 \neq -1$ and $n_1, \varpi \epsilon \text{elt}`\text{P}$, the first term of the stretch is the sequent of an $\omega_{\mu_2}$ and therefore is an $n_1, \mu_2$ element. If $\nu_2 \neq -1$ and $\varpi, m_1 \epsilon \text{elt}`\text{P}$, the last term of the stretch is the predecessor of the series

$$\ldots xs_\xi, \ldots xs_2, xs_1 \qquad \xi < \omega_{\nu_2},$$

where

$$\ldots \; s_\xi \; \ldots \; s_2 \; s_1 \qquad \xi < \omega_{\nu_2}$$

is an $^*\omega_{\nu_2}$ having y as its predecessor and contained in Q. The term then is a ν_2, m_1 element. If $\mu_2 = -1$, so that y has an immediate predecessor y', the first term of the stretch $x_0 y$ will be immediately preceded by $x_\Omega y'$ if P has a last term x_Ω, and so will be an n_1, μ_2 element as before and will be the sequent of such a series as

$$c_1 y', c_2 y', \ldots c_\zeta y' \ldots \qquad \zeta < \omega_{m_1},$$

where

$$c_1 \; c_2 \; \ldots c_\zeta \; \ldots \qquad \zeta < \omega_{m_1}$$

is an ω_{m_1} confinal with P, and therefore will be an n_1, m_1 element if P has no last term. Again, if $\nu_2 = -1$ and $\varpi, m_1 \epsilon \text{elt}`\text{P}$, the last term of the stretch is a ν_2, m_1 element if P has a first term, and an n_1, m_1 element if P has no first term.

If $n_1, \varpi \epsilon \text{gap}`\text{P}$, so that P has no first term, the stretch will be coinitial with an $^*\omega_{n_1}$

$$\ldots d_\xi y, \ldots d_2 y, d_1 y \qquad \xi < \omega_{n_1}, \quad . \quad . \quad . \quad (1)$$

where

$$\ldots d_\xi \; \ldots d_2 \; d_1 \qquad \xi < \omega_{n_1}$$

is an $^*\omega_{n_1}$ coinitial with P. It is to be remarked that $n_1 \neq -1$, since P has no beginning †. This series, together with the series

$$xr_1 \, xr_2 \ldots xr_\zeta \ldots \qquad \zeta < \mu_2, \quad . \quad . \quad . \quad . \quad (2)$$

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† *Cp.* "On the Structure of Serial Relations," Phil. Mag., November 1929.

if $\mu_2 \neq -1$, will give an n_1, μ_2 gap. If $\varpi, m_1 \epsilon \text{gap}'\,\text{P}$, so that P has no last term, the stretch will be confinal with such an ω_{m_1} as

$$c_1y\; c_2y \dots c_\zeta y \dots \qquad \zeta < \omega_{m_1}. \quad . \quad . \quad . \quad (3)$$

And again it is to be remarked that $m_1 \neq -1$ since P has no end†. This series, together with the series

$$\dots xs_\xi \dots xs_2\; xs_1 \qquad \xi < \omega_{\nu_2}, \quad . \quad . \quad . \quad . \quad (4)$$

if $\nu_2 \neq -1$, will give a ν_2, μ_1 gap. But when P has no first term, if $\mu_2 = -1$ so that y has an immediate predecessor y', if P has a last term x_Ω, $x_\Omega y'$ will be the predecessor of such an ω_{m_1} as

$$c_1y'\; c_2y' \dots c_\zeta y' \dots \qquad \zeta < \omega_{m_1}. \quad . \quad . \quad . \quad (5)$$

It will therefore be an n_1, m_1 element. If P has no last term, (5) and (1) will give together an n_1, m_1 gap. Similarly, if P has no last term, if $\nu_2 = -1$, we shall have an n_1, m_1 element if P has a first term, and otherwise an n_1, m_1 gap.

§ 2. Suppose Q has a first term y_0, and let us consider the character of the stretch of Q × P, for which the Q-term is y_0. If P has a last term x_Ω, the stretch will have a last term $x_\Omega y_0$, which limits the series

$$c_1y_0, c_2y_0, \dots c_\zeta y_0 \dots \qquad \zeta < \omega_{m_1} \quad \text{if } m_1 \neq -1$$

and the series

$$\dots xf_\xi, \dots xf_2, xf_1 \qquad \xi < \omega_{n_2} \quad \text{if } n_2 \neq -1,$$

where

$$\dots \quad f_\xi \dots \quad f_2 \quad f_1 \qquad \xi < \omega_{n_2}$$

is an $^*\omega_{n_2}$ coinitial with the Q-series. If $m_1 \neq -1$, $n_2 \neq -1$, $x_\Omega y_0$ will therefore be an n_2, m_1 element. If $m_1 = -1$, so that x_Ω has an immediate predecessor x_Ω', $x_\Omega y_0$ will be immediately preceded by $x_\Omega' y_0$ and will be an $n_2, -1$ element, and so an n_2, m_1 element as before. If $n_2 = -1$, so that y_0 has an immediate successor y_0', if P has a first term x_0, $x_\Omega y_0$ will be immediately followed by $x_0 y_0'$, and so will be an n_2, m_1 element as before. If $n_2 = -1$ and P has no first term, $x_\Omega y_0$ will limit such a series as

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† *Loc. cit.*

$$\ldots d_\xi y_0' \ldots d_2 y_0' \, d_1 y_0 \qquad \xi < \omega_{n_1};$$

and so, instead of an n_2, m_1 element, there will be an n_1, m_1 element. If there is no last term in the P-series, there will be no last term in the stretch. Instead, there will be an ω_{m_1} confinal with it,

$$c_1 y_0' \, c_2 y_0 \ldots c_\zeta y_0 \ldots \qquad \zeta < \omega_{m_1}, \quad . \quad . \quad . \quad (6)$$

and $m_1 \neq -1$, as P has no last term. This series, together with such a series as

$$\ldots x f_\xi \ldots x f_2 \, x f_1 \qquad \xi < \omega_{n_2},$$

if $n_2 \neq -1$, forms an n_2, m_1 gap. If $n_2 = -1$, so that y_0 has an immediate successor y_0', and if P has a first term x_0, $x_0 y_0'$ will limit the series (6) and will be the predecessor of such a series as

$$\ldots d_\xi y_0' \ldots d_2 y_0' \, d_1 y_0' \qquad \xi < \omega_{n_1} \; n_1 \neq -1, \quad . \quad (7)$$

or $x_0' y_0'$ if x_0 has an immediate follower x_0'. There will therefore be an n_1, m_1 element instead of an n_2, m_1 gap. If $n = -1$ and P has no first term, instead of the n_2, m_1 gap there will be the n, m_1 gap formed by the series (6) and (7).

The stretch will have a first term if x_0 exists. This term $x_0 y_0$ will be the predecessor of such a series as

$$\ldots d_\xi y_0, \ldots d_2 y_0, \, d_1 y_0 \qquad \xi > \omega_{n_1}, \quad . \quad . \quad . \quad (8)$$

and so will be an n_1, ϖ element, since it is the first term of the series $Q \times P$ as well as of the stretch. When x_0 does not exist, the stretch (and the series) will be coinitial with the series (8), and in consequence there will be an n_1, ϖ gap.

We get, therefore, the following characters of the series $Q \times P$, if y_0 exists:—

If x_0 exists, there is an n_1, ϖ element; if it does not, there is an n_1, ϖ gap. If x_Ω exists, there is an n_2, m_1 element which, in the exceptional case when $n_2 = -1$, becomes an n_1, m_1 element if x_0 does not exist. If x_Ω does not exist, there is an n_2, m_1 gap which, in the exceptional case when $n_2 = -1$, becomes an n_1, m_1 element if x_0 exists and an n_1, m_1 gap if x_0 does not exist.

Corresponding results can be obtained by condensing the stretch (if there is one) which has y_Ω as its Q-term.

§ 3. We may sum up the results so far obtained.

1. $\nu_1, \mu_1 \epsilon$ elt‘ P.

2. If n_1, ϖ ; $\varpi, m_1 \epsilon$ elt‘ P, n_1, μ_2 ; $\nu_2, m_1 \epsilon$ elt‘ Q × P.
   - (*a*) If also $n_2, \varpi \epsilon$ elt‘ Q, n_2, m_1 ; $n_1, \varpi \epsilon$ elt‘ Q × P in addition.
   - (*b*) If also $\varpi, m_2 \epsilon$ elt‘ Q, n_1, m_1 ; $\varpi, m_1 \epsilon$ elt‘ Q × P in addition.

3. If $n_1, \varpi \epsilon$ elt‘ P, $\varpi, m_1 \epsilon$ gap‘ P, $n_1, \mu_2 \epsilon$ elt‘ Q × P, $\nu_2, m_1 \epsilon$ gap‘ Q × P.
   - (*a*) If $n_2, \varpi \epsilon$ elt‘ Q, $n_1, \varpi \epsilon$ elt‘ Q × P, $n_2, m_1 \epsilon$ gap‘ Q × P in addition.
   - (*b*) If $\varpi, m_2 \epsilon$ elt‘ Q, $n_1, m_2 \epsilon$ elt‘ Q × P, $\varpi, m_1 \epsilon$ gap‘ Q × P.

4. If $\varpi, m_1 \epsilon$ elt‘ P, $n_1, \varpi \epsilon$ gap‘ P, $\nu_2, m_1 \epsilon$ elt‘ Q × P, $n_1, \mu_2 \epsilon$ gap‘ Q × P.
   - (*a*) If $n_2, \varpi \epsilon$ elt‘ Q, $n_2, m_1 \epsilon$ elt‘ Q × P, $n_1, \varpi \epsilon$ gap‘ Q × P.
   - (*b*) If $\varpi, m_1 \epsilon$ elt‘ Q, $\varpi, m_1 \epsilon$ elt‘ Q × P, $n_1, m_2 \epsilon$ gap‘ Q × P.

5. If n_1, ϖ ; $\varpi, m_1 \epsilon$ gap‘ P, ν_2, m_1 ; $n_1, \mu_2 \epsilon$ gap‘ Q × P.
   - (*a*) If $n_2, \varpi \epsilon$ elt‘ Q, n_1, ϖ ; $n_2, m_1 \epsilon$ gap‘ Q × P.
   - (*b*) If $\varpi, m_2 \epsilon$ elt‘ Q, ϖ, m_1 ; $n_1, m_2 \epsilon$ gap‘ Q × P.

The conventions with regard to the interpretation of the special cases when the variables take the value -1 are as follows:—In 3 and 4, if μ_2 or ν_2, or m_2 or n_2, is equal to -1, replace the character in which it occurs by the element with m_1 substituted for μ_2 or m_2 and n_1 for ν_2 or n_2. In 5, for ν_2 or n_2, or μ_2 or m_2, if they are equal to -1, put n_1, m_1 respectively.

§ 4. The gaps of P, except those which contain ϖ, are represented in Q × P, since Q × P has stretches which are ordinally similar to P. Consider now the gap of Q.

The series

$$xt_1^*, xt_2^*, \ldots xt_\zeta \ldots \ldots \ldots \qquad \zeta < \omega_{\rho_2}$$

$$\ldots \quad \ldots \quad \ldots, xu_\xi \ldots xu_2\, xu_1 \qquad \xi < \omega_{\sigma_2}$$

define a gap in Q × P, just as the series

$$t_1 \;\; t_2 \;\ldots\; t_\zeta \ldots \ldots \qquad \zeta < \omega_{\rho_2}$$

$$\ldots \ldots \ldots u_\xi\; u_2\; u_1 \qquad \zeta < \omega_{\sigma_2}$$

define a gap in the Q series. And there are no exceptional cases, since ρ_2, σ_2 can neither of them be equal to -1. The gaps of Q therefore occur in $Q \times P$ as well as the gaps of P.

§ 5. The only other question to be considered is the nature of the beginning and end of $Q \times P$. It is plain that only if P and Q have beginnings, $Q \times P$ has a beginning This beginning will be the couple $x_0 y_0$, which is the predecessor of the $^*\omega_{n_1}$

$$\dots c_\xi y_0 \dots c_2 y_0 \; c_1 y_0 \qquad \xi < \omega_{n_1}, \quad . \quad . \quad . \quad (9)$$

even if $n_1 = -1$. n_1, ϖ is therefore an element of $Q \times P$. And if x_Ω and y_Ω exist, $x_\Omega y_\Omega$ will be an ϖ, m_1 element even if $m_1 = -1$.

If x_0 does not exist and y_0 exists, there will be no beginning, but the $^*\omega_{n_1}$ (9) will be coinitial with $Q \times P$. And $n_1 \neq -1$, since x_0 does not exist. $Q \times P$ therefore has an n_1, ϖ gap.

If y_0 does not exist, the series

$$\dots x e_\xi \dots x e_2, \; x e_1 \qquad \xi < \omega_{n_2},$$

where

$$\dots \; e_\xi \dots \; e_2 \;\; e_1 \qquad \xi < \omega_{n_2}$$

is an $^*\omega_{n_2}$ coinitial with Q, is coinitial with $Q \times P$. $n_2 \neq -1$, since y_0 does not exist. $Q \times P$ therefore contains an n_2, ϖ gap.

Corresponding results may be obtained by considering the nature of the end of $Q \times P$.

The results of this § may be summed up.

If $n_1, \varpi \in$ elt‘P, if $n_2, \varpi \in$ elt‘Q, $n_1, \varpi \in$ elt‘$Q \times P$,
if $n_2, \varpi \in$ gap‘Q, $n_2, \varpi \in$ gap‘$Q \times P$.

If $n_1, \varpi \in$ gap‘P, if $n_2, \varpi \in$ elt‘Q, $n_1, \varpi \in$ gap‘$Q \times P$,
if $n_2, \varpi \in$ gap‘Q, $n_2, \varpi \in$ gap‘$Q \times P$.

If $\varpi, m_1 \in$ elt‘P, if $\varpi, m_2 \in$ elt‘Q, $\varpi, m_1 \in$ elt‘$Q \times P$,
if $\varpi, m_2 \in$ gap‘Q, $\varpi, m_2 \in$ gap‘$Q \times P$.

If $\varpi, m_1 \in$ gap‘P, if $\varpi, m_2 \in$ elt‘Q, $\varpi, m_1 \in$ gap‘$Q \times P$,
if $\varpi, m_2 \in$ gap‘Q, $\varpi, m_2 \in$ gap‘$Q \times P$.

§ 6. The characters of the series $Q \times P$ are therefore as follows :—

In all cases $\nu_1, \mu_1 \epsilon \text{elt}' Q \times P$, σ_1, ρ_1, $\sigma_2, \rho_2 \epsilon \text{gap}' P$. In addition, the series has the characters indicated in the following table. On the left in each are the elements, on the right the gaps.

Q		ν_2, μ_2 ; ϖ, m_2 n_2, ϖ	σ_2, ρ_2	ν_2, μ_2 ; n_2, ϖ	σ_2, ρ_2 ϖ, m_2	ν_2, μ_2 ; ϖ, m_2	σ_2, ρ_2 n_2, ϖ	ν_2, μ_2 ;	σ_2, ρ_2 ϖ, m_2 n_2, ϖ
P									
ν_1, μ_1 ; ϖ, m_1 n_1, ϖ	σ_1, ρ_1	n_1, μ_2 ; ν_2, m_1 n_1, m_2 n_2, m_1 n_1, ϖ ϖ, m_1		n_1, μ_2 ; ν_2, m_1 n_2, m_1 n_1, ϖ	ϖ, m_2	n_1, μ_2 ; ν_2, m_1 n_1, m_2 ϖ, m_1	n_2, ϖ	n_1, μ_2 ; $\nu_2\ m_1$	n_2, ϖ $\varpi\ m_2$
ν_1, μ_1 ; n_1, ϖ	σ_1, ρ_1 ϖ, m_1	n_1, μ_2 † ; n_1, m_2 † n_1, ϖ	ν_2, m_1 § n_2, m_1 § ϖ, m_1	n_1, μ_2 † ; n_1, ϖ	ν_2, m_1 § n_2, m_1 § ϖ, m_2	n_1, μ_2 † ; n_1, m_2 †	ν_2, m_1 § n_2, ϖ ϖ, m_1	n_1, μ_2 † ;	ν_2, m_1 § n_2, ϖ ϖ, m_2
ν_1, μ_1 ; ϖ, m_1	σ_1, ρ_1 n_1, ϖ	ν_2, m_1 * n_2, m_1 * ϖ, m_1	; n_1, μ_2 ‡ n_1, m_2 ‡ n_1, ϖ	ν_2, m_1 * n_2, m_1 *	; n_1, μ_2 ‡ n_1, ϖ ϖ, m_2	ν_2, m_2 * ϖ, m_1	; n_1, μ_2 ‡ n_1, m_2 ‡ n_2, ϖ	ν_2, m_1 *	; n_1, μ_2 ‡ n_2, ϖ ϖ, m_2
ν_1, μ_1 ;	σ_1, ρ_1 ϖ, m_1 n_1, ϖ		; n_1, μ_2 † ν_2, m_1 * n_1, m_2 † n_2, m_1 * n_1, ϖ ϖ, m_1		; n_1, μ_2 † ν_2, m_1 * n_2, m_1 * n_1, ϖ ϖ, m_2		; n_1, μ_2 † ν_2, m_1 * n_1, m_2 † n_2, ϖ ϖ, m_1		; n_1, μ_2 † ν_2, m_1 * n_2, ϖ ϖ, m_2

* If ν_2 or n_2 is equal to -1, substitute for it n_1.

† If μ_2 or m_2 is equal to -1, substitute for it m_1.

§ If ν_2 or n_2 is equal to -1, substitute for it n_1 and transfer character to elements.

‡ If μ_2 or m_2 is equal to -1, substitute for it m_1 and transfer character to elements.

§ 7. Our general formula gives interesting results in particular cases. If $P, Q \epsilon \text{Ded}$, P and Q have no gaps ‖, and therefore $Q \times P$ has no gaps, and so is Dedekindian. Therefore

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‖ See "On the Structure of Serial Relations," *loc. cit.*

$$P, Q \,\epsilon\, \mathrm{Ded} \,.\supset.\, Q \times P \,\epsilon\, \mathrm{Ded}.$$

If $Q \times P \,\epsilon\, \mathrm{Ded}$, it is clear from the table that $Q, P \,\epsilon\, \mathrm{Ded}$. Hence

$$P, Q \,\epsilon\, \mathrm{Ded} \,.\equiv.\, Q \times P \,\epsilon\, \mathrm{Ded}.$$

Suppose $Q \times P \sim\epsilon\, \mathrm{Ded}$. $Nr‘Q \times P + 1 \subset \mathrm{Ded}$, so that $Q \times P$, though not itself Dedekindian, would be Dedekindian with the addition of a last term. Then $Q \times P$ would have no gaps except one with ϖ on the left. Hence P and Q have no gaps except possibly ones with ϖ on the left. And if neither has a gap with ϖ on the left, then $Q \times P$ would be Dedekindian. Hence either P or Q must have a gap with ϖ on the left, and neither may have any other gaps. Therefore either P has no gaps and Q has a gap ϖ, m_2 only, or P has a gap ϖ, m_1 only and $\nu_2 = n_2 = -1$, and Q has no gaps except possibly one with ϖ on the left. Thus, either

$$P \,\epsilon . \mathrm{Ded} \,.\, Nr‘Q + 1 \subset \mathrm{Ded} \,.\, Q \sim\epsilon\, \mathrm{Ded},$$

or

$$Nr‘P + 1 \subset \mathrm{Ded} \,.\, P \sim\epsilon\, \mathrm{Ded} \,.\, Q \,\epsilon\, \Omega.$$

The converse is easily verified from the table, and so it is established that

$$\begin{aligned} &Nr‘Q \times P + 1 \subset \mathrm{Ded} \,.\, Q \times P \sim\epsilon\, \mathrm{Ded} \\ &\qquad :\equiv: P \,\epsilon\, \mathrm{Ded} \,.\, Nr‘Q \times 1 \subset \mathrm{Ded} \,.\, Q \sim\epsilon\, \mathrm{Ded} \,.\vee. \\ &\qquad\qquad Nr‘P + 1 \subset \mathrm{Ded} \,.\, P \sim\epsilon\, \mathrm{Ded} \,.\, Q \,\epsilon\, \Omega. \end{aligned}$$

7.1[†]

We also have

$$\begin{aligned} &1 + Nr‘Q \times P \subset \mathrm{Ded} \,.\, Q \times P \sim\epsilon\, \mathrm{Ded} \\ &\qquad :\equiv: P \,\epsilon\, \mathrm{Ded} \,.\, 1 + Nr‘Q \subset \mathrm{Ded} \,.\, Q \sim\epsilon\, \mathrm{Ded} \,.\vee. \\ &\qquad\qquad 1 + Nr‘P \subset \mathrm{Ded} \,.\, P \sim\epsilon\, \mathrm{Ded} \,.\, Q \,\epsilon\, \Omega. \end{aligned}$$

. . . 7.2[†]

§ 8. If $Q \times P$ is well-ordered[‡], it must have a first term, all its element characters must have -1 on the left, and there must be no gaps except possibly one with ϖ on the left. The existence of the first term of $Q + P$ makes it necessary that P and Q should have first terms, and since Q × P has no gaps except possibly one with ϖ on the left, P and Q have no gaps except possibly ones with ϖ on the left. Since every element character of Q × P has -1 on the left,

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[†] It is clear that this proposition is independent of the assumption made at the beginning of this paper that an element cannot be the sequent of an ω_m and an ω_n unless $m = n$.

[‡] See my paper, *loc. cit.*

$$\nu_1 = n_1 = \nu_2 = n_2 = -1.$$

Hence $n_1 = \nu_1 = -1$ and P has no gaps except possibly one with ϖ on the left, and $n_2 = \nu_2 = -1$ and Q has no gaps except possibly one with ϖ on the left. Hence $P, Q \epsilon \Omega$. The converse is easily established, and it follows that

$$P, Q \epsilon \Omega . \equiv . QP \tau \Omega. \quad \ldots \ldots \quad 8.1$$

CVI. *On Levi-Civita's Modification of Einstein's Unified Field Theory.* By G. C. McVittie, *M.A.* (*Edin.*), *Christ's College, Cambridge* †.

§ I. *Introduction and Summary.*

PROF. LEVI-CIVITA ‡ has modified Prof. Einstein's Unified Field Theory ‖ of gravitation and electromagnetism by discarding the concept of "parallelism at a distance with respect to 4 orthogonal vectors of reference," which is the basis of the latter's theory, and obtaining a complete description of gravitational and electromagnetic phenomena by means of the Ricci Coefficients of Rotation of 4 orthogonal congruences of lines which, at each point, define 4 orthogonal vectors of reference in a Riemann space.

In the present paper we apply Prof. Levi-Civita's theory to a particular case, *i. e.*, one in which an exact solution of the usual gravitational and electromagnetic equations of the relativity theory is known, and we compare the results so obtained with those arrived at in a previous paper ¶ by the use of Prof. Einstein's theory.

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† Communicated by Prof. E. T. Whittaker, F.R.S.

‡ *Berliner Sitzungberichte*, viii.–x. p. 137 (1929).

‖ *Berliner Sitzungberichte*, i. p. 2 (1929).

¶ G. C. McVittie, 'On Einstein's Unified Field Theory,' Proc. Roy. Soc. A, cxxiv. p. 366.

In § II. we obtain the congruences for this case and show that the 4 orthogonal vectors of reference which these congruences establish at any arbitrary point are substantially the same as those which are obtained by the use of Prof. Einstein's theory.

In § III. we show that the electromagnetic potential vector in the field can be given a geometrical interpretation in Prof. Levi-Civita's theory, which bears a very close analogy to that given to it in Prof. Einstein's theory. In Prof. Levi-Civita's theory, however, this interpretation appears to hold in special cases only, of which ours is one. At any rate, we have not found a general proof that the relation

$$F_{\mu\nu}=\frac{\partial\phi_\mu}{\partial x_\nu}-\frac{\partial\phi_\nu}{\partial x_\mu}$$

between the electric force tensor $F_{\mu\nu}$ and the potential vector ϕ_μ also holds between the geometrical quantities which represent them.

§ II. *Calculation of the Congruences.*

The special case to which we apply Prof. Levi-Civita's theory is that of the gravitational field of an electrostatic field of uniform direction †. The metric and the electromagnetic potential of this field are, respectively,

$$\left.\begin{aligned} ds^2 &= e^{\alpha x_1}dx_4{}^2-e^{-2\alpha x_1}dx_1{}^2-e^{-\alpha x_1}dx_2{}^2-e^{-\alpha x_1}dx_3{}^2, \\ \phi_4 &= \frac{1}{2\sqrt{\pi}}e^{\frac{1}{2}\alpha x_1}, \quad \phi_1=0, \quad \phi_2=0, \quad \phi_3=0. \end{aligned}\right\} \quad (1)$$

In this field the electromagnetic force which would be measured at an arbitrary point $P(\equiv\tau, a, b, c)$ in the field is an electric force in the direction of the x_1-axis, constant at the point and of amount $\alpha e^{\alpha a}/4\sqrt{\pi}$.

Let, then, $\lambda^\nu(\nu=1, 2, 3, 4)$ denote the contravariant parameters of the sth congruence ($s=1, 2, 3, 4$), and let ${}^s\lambda_\nu$ denote the covariant moments of the same congruence ‡. [We have altered the notation for the parameters and moments to bring it into line with that of Prof. Einstein's theory. Indices denoting the congruence are written to the left of the " λ," those denoting the coordinates to the right.]

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† G. C. McVittie, *loc. cit.*

‡ Levi-Civita, 'Absolute Differential Calculus,' Chap. x.

If, now, the $g_{\mu\nu}$ define the metric, we have the relations

$$ {}^i\lambda_\nu = \sum_{\rho=1}^{4} g_{\rho\nu}\, {}_i\lambda^\rho $$

and

$$ g_{\mu\nu} = \sum_{i=1}^{4} e_i\, {}^i\lambda_\mu\, {}^i\lambda_\nu, \quad \ldots\ldots\ldots \quad (2) $$

where $e_i = \pm 1.$

In the case of the field given by (1) we have

$$ e_4 = 1, \qquad e_1 = e_2 = e_3 = -1. $$

We now assume that the moments of the congruences are:

$$ \begin{array}{llllll} ({}^4\lambda_4, & {}^4\lambda_1, & 0, & 0\,) & \text{for the congruence} & \text{“ 4,”} \\ ({}^1\lambda_4, & {}^1\lambda_1, & 0, & 0\,) & \text{,, ,, ,,} & \text{“ 1,”} \\ (\,0, & 0, & {}^2\lambda_2, & 0\,) & \text{,, ,, ,,} & \text{“ 2,”} \\ (\,0, & 0, & 0, & {}^3\lambda_3) & \text{,, ,, ,,} & \text{“ 3,”} \end{array} $$

that all these ${}^i\lambda_\nu$ are functions of x_1 alone, and that

$$ {}^2\lambda_2 = {}^3\lambda_3. $$

With these values for the moments the ten equations (2) reduce to the five:

$$ \left. \begin{aligned} e^{ax_1} &= {}^4\lambda_4{}^2 - {}^1\lambda_4{}^2, \\ -e^{-2ax_1} &= {}^4\lambda_1{}^2 - {}^1\lambda_1{}^2, \\ -e^{-ax_1} &= -{}^2\lambda_2{}^2, \\ -e^{-ax_1} &= -{}^2\lambda_3{}^2, \\ 0 &= {}^4\lambda_1\, {}^4\lambda_4 - {}^1\lambda_1\, {}^1\lambda_4. \end{aligned} \right\} \quad \ldots\ldots \quad (2.1) $$

We note that these equations are also the conditions of orthogonality of the four congruences.

The solutions are:

$$ \left. \begin{aligned} {}^4\lambda_4 &= e^{\frac{1}{2}ax_1}\cosh v, & {}^1\lambda_4 &= e^{\frac{1}{2}ax_1}\sinh v, \\ {}^4\lambda_1 &= e^{-ax_1}\sinh v, & {}^1\lambda_1 &= e^{-ax_1}\cosh v, \\ {}^2\lambda_2 &= e^{-\frac{1}{2}ax_1}, & {}^3\lambda_3 &= e^{-\frac{1}{2}ax_1}. \end{aligned} \right\} \quad \ldots \quad (3) $$

where v is an undetermined function of x_1.

The parameters are, therefore

$$\left.\begin{aligned} {}_4\lambda^4 &= e^{-\frac{1}{2}\alpha x_1}\cosh v, & {}_1\lambda^4 &= e^{-\frac{1}{2}\alpha x_1}\sinh v, \\ {}_4\lambda^1 &= -e^{\alpha x_1}\sinh v, & {}_1\lambda^1 &= -e^{\alpha x_1}\cosh v, \\ {}_2\lambda^2 &= -e^{\frac{1}{2}\alpha x_1}, & {}_3\lambda^3 &= -e^{\frac{1}{2}\alpha x_1}. \end{aligned}\right\} \quad . \quad (4)$$

To find v we calculate the geometrical quantities which represent the electromagnetic force tensor and equate them to the known values of the components of this tensor in the field (1). This is done as follows.

The Christoffel symbols for the metric (1) which do not vanish are:

$$\begin{aligned} \left\{ {12 \atop 2} \right\} &= -\frac{\alpha}{2}, & \left\{ {22 \atop 1} \right\} &= \frac{\alpha}{2}e^{\alpha x}, \\ \left\{ {13 \atop 3} \right\} &= -\frac{\alpha}{2}, & \left\{ {33 \atop 1} \right\} &= \frac{\alpha}{2}e^{\alpha x_1}, \\ \left\{ {14 \atop 4} \right\} &= \frac{\alpha}{2}, & \left\{ {44 \atop 1} \right\} &= \frac{\alpha}{2}e^{3\alpha x_1}, \end{aligned}$$

$$\left\{ {11 \atop 1} \right\} = -\alpha.$$

The coefficients of rotation are defined by

$$\gamma_{ikt} = \sum_{\nu,\rho=1}^{4} {}^i\lambda_{\nu\rho}\, {}_k\lambda^\nu\, {}_t\lambda^\rho. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Hence, to calculate them, we must find the covariant derivatives, ${}^i\lambda_{\nu\rho}$, of the moments. The non-zero ones are:

$$\begin{aligned} {}^4\lambda_{11} &= e^{-\alpha x_1} v' \cosh v, & {}^4\lambda_{14} &= -\frac{\alpha}{2}e^{\frac{1}{2}\alpha x_1}\cosh v, \\ {}^4\lambda_{41} &= e^{\frac{1}{2}\alpha x_1} v' \sinh v, & {}^4\lambda_{44} &= -\frac{\alpha}{2}e^{2\alpha x_1}\sinh v, \\ {}^4\lambda_{22} &= -\frac{\alpha}{2}\sinh v, & {}^4\lambda_{33} &= -\frac{\alpha}{2}\sinh v. \end{aligned}$$

$$\begin{aligned} {}^1\lambda_{41} &= e^{\frac{1}{2}\alpha x_1} v' \cosh v, & {}^1\lambda_{14} &= -\frac{\alpha}{2}e^{\frac{1}{2}\alpha x_1}\sinh v, \\ {}^1\lambda_{11} &= e^{-\alpha x_1} v' \sinh v, & {}^1\lambda_{44} &= -\frac{\alpha}{2}e^{2\alpha x_1}\cosh v, \\ {}^1\lambda_{22} &= -\frac{\alpha}{2}\cosh v. & {}^1\lambda_{33} &= -\frac{\alpha}{2}\cosh v. \end{aligned}$$

$$ {}^{3}\lambda_{13} = \frac{\alpha}{2} e^{-\frac{1}{2}\alpha x_1}, \qquad {}^{2}\lambda_{12} = \frac{\alpha}{2} e^{-\frac{1}{2}\alpha x_1}, $$

where

$$ v' = \frac{dv}{dx_1}. $$

On substitution into (5) we get that the non-zero coefficients are:

$$ \gamma_{414} = -\gamma_{144} = e^{\alpha x_1}\left(v' \sinh v + \frac{\alpha}{2} \cosh v\right), $$

$$ \gamma_{411} = -\gamma_{141} = e^{\alpha x_1}\left(v' \cosh v + \frac{\alpha}{2} \sinh v\right), $$

$$ \gamma_{422} = -\gamma_{242} = -\frac{\alpha}{2} e^{\alpha x_1} \sinh v, $$

$$ \gamma_{433} = -\gamma_{343} = -\frac{\alpha}{2} e^{\alpha x_1} \sinh v, $$

$$ \gamma_{133} = -\gamma_{313} = -\frac{\alpha}{2} e^{\alpha x_1} \cosh v, $$

$$ \gamma_{122} = -\gamma_{212} = -\frac{\alpha}{2} e^{\alpha x_1} \cosh v. $$

Now it is known that a set of 4 orthogonal congruences in a 4-dimensional Riemann space define 4 unit vectors of reference at each point and that any arbitrary tensor in the space can be defined by of its "invariants" with regard to these 4 unit vectors †. For instance, if A^{μ} denote the contravariant components of a vector referred to the coordinates, and $*A^{m}$ the corresponding "invariant," we have

$$ *A^{m} = \sum_{\nu=1}^{4} e_m {}^{m}\lambda_{\nu} A^{\nu}, $$

and similarly

$$ *A_{m} = \sum_{\nu=1}^{4} e_m {}_{m}\lambda^{\nu} A_{\nu}. $$

Instead of the term "invariants" we shall use the term "lattice-tensor," and denote such lattice-tensors by means of an asterisk.

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† Levi-Civita, 'Absolute Differential Calculus,' p. 265.

We now calculate the lattice-tensor

$$\psi^*_{ik}=\sum_{t=1}^{4} e_t\,{}_t\lambda^\rho \frac{\partial\gamma_{ikt}}{\partial x_\rho}=-{}_1\lambda^1\frac{d\gamma_{ik1}}{dx_1}+{}_4\lambda^1\,\frac{d\gamma_{ik4}}{dx_1}$$

in our case.

We get that the only non-zero components are

$$\psi^*_{41}=-\psi^*_{14}=e^{\alpha x_1}\cosh v\frac{d}{dx_1}\left\{e^{\alpha x_1}(v'\cosh v+\frac{\alpha}{2}\sinh v)\right\}$$
$$-e^{\alpha x_1}\sinh v\,\frac{d}{dx_1}\left\{e^{\alpha x_1}(v'\sinh v+\frac{\alpha}{2}\cosh v)\right\}. \quad (6)$$

Now Prof. Levi-Civita identifies the lattice-tensor ψ^*_{ik} with the lattice-tensor F^*_{ik}, *i. e.*, with the lattice-tensor corresponding to the electromagnetic force tensor $F_{\mu\nu}$. The relation is

$$F^*_{ik}=a\psi^*_{ik}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where a = constant with the dimensions of an electric charge.

In the case of the field given by (1) we have that

$$F_{41}=-F_{14}=\frac{\alpha}{4\sqrt{\pi}}\,e^{\frac{1}{2}\alpha x_1},$$

all the other components being zero.

Hence, since

$$F^*_{ik}=\sum_{\mu,\nu=1}^{4} e_i e_k F_{\mu\nu}\,{}_i\lambda^\mu\,{}_k\lambda^\nu,$$

we have

$$F^*_{41}=-F^*_{14}=\frac{\alpha}{4\sqrt{\pi}}\,e^{\alpha x_1}.$$

Hence, substituting this value into (7), and thence into (6), we get the equation for determining v, viz.,

$$\frac{\alpha}{4a\sqrt{\pi}}=\frac{d}{dx_1}(e^{\alpha x_1}v')+\frac{\alpha}{2}\,v'e^{\alpha x_1},$$

which gives

$$v=\frac{1}{2a\alpha\sqrt{\pi}}\left(-e^{-\alpha x_1}+\frac{2}{3}\,e^{-\frac{3}{2}\alpha x_1}+\frac{1}{3}\right), \quad . \quad . \quad (8)$$

the constants of integration being adjusted so that $v=0$ when $\alpha=0$.

Hence, the congruences whose parameters and moments are given by (3), (4), and (8) are completely determined by the field (1), and conversely, by means of equations (2.1), (5), and (6), the congruences, if known, would exactly determine the field. Also these values of the parameters and moments rigorously satisfy the field equations † given for them by Prof. Levi-Civita (the equations II. being identities and the field (1) having been obtained as a solution of equations I.).

If we compare the solution given by equations (3), (4), and (8) with that obtained by the use of Prof. Einstein's theory ‡, we see that they are identical, except for the presence of the quantity $\sqrt{(-1)}$ in the latter case. This, however, merely arises from the fact that in the present work we have employed the quantities $e_i = \pm 1$ in the calculation, with the result that imaginary quantities do not enter into the final statement of the solution.

We therefore have, finally, *the congruences of Prof. Levi-Civita's theory establish at each point the same four orthogonal unit vectors which are used by Prof. Einstein to define "parallelism at a distance" in the field.*

§ III. *The Geometrical Interpretation of the Electromagnetic Vector Potential.*

This similarity between the solutions on the two theories suggested that the geometrical quantities of the present theory, corresponding to those which defined the electromagnetic potential vector in Einstein's theory, would play the same part in the present one. We therefore calculate the vector

$$\chi_\rho = \sum_{i,\nu=1}^{4} e_i \, \lambda^\nu ({}^i\lambda_{\rho\nu} - {}^i\lambda_{\nu\rho}) = \sum_{i,\nu=1}^{4} e_i \, {}_i\lambda^\nu \left(\frac{\partial\, {}^i\lambda_\rho}{\partial x_\nu} - \frac{\partial\, {}^i\lambda_\nu}{\partial x_\rho} \right). \qquad (9)$$

On substitution into (9) from (3), (4), and (8), we get

$$\left.\begin{aligned} \chi_4 &= \frac{1}{2a\sqrt{\pi}} (e^{\frac{1}{2}\alpha\tau_1} - 1), \\ \chi_1 &= \frac{\alpha}{2}, \\ \chi_2 &= \chi_3 = 0. \end{aligned}\right\} \quad . \; . \; . \; . \; . \qquad (10)$$

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† Levi-Civita, *Berliner Sitzungberichte*, viii.–x. p. 137 (1929), equations I. and II.

‡ G. C. McVittie, *loc. cit.* equations (2.6), (2.7), and (3.3).

If, now (as had to be done in the case of Einstein's theory when applied to the field (1)), the electromagnetic potential vector in (1) is taken to be

$$\phi_4 = \frac{1}{2\sqrt{\pi}}\left(e^{\frac{1}{2}\alpha x_1} - 1\right), \quad \phi_1 = \frac{\alpha}{2a}, \quad \phi_2 = 0, \quad \phi_3 = 0,$$

by adding the constants $-1/2\sqrt{\pi}$ and $\alpha/2a$ to ϕ_4 and ϕ_1 respectively, we see that we can make the identification

$$\phi_4 = a\chi_4, \quad \phi_1 = a\chi_1, \quad \phi_2 = a\chi_2, \quad \phi_3 = a\chi_3. \quad . \quad (11)$$

The vector χ has the following geometrical interpretation:—

By the definition (5) of the γ_{ikt} we have that

$$\gamma_{ikt} - \gamma_{itk} = \sum_{\nu,\rho=1}^{4} {}_k\lambda^\nu {}_t\lambda^\rho \left\{ \frac{\partial\, {}^i\lambda_\nu}{\partial x_\rho} - \frac{\partial\, {}^i\lambda_\rho}{\partial x_\nu} \right\}.$$

Put $i=k$, multiply by e_i and e_t, sum with respect to i, and note that $\gamma_{iit} = 0$ for all i. We have

$$\left.\begin{aligned} \sum_{i=1}^{4} e_t e_i \gamma_{iti} &= \sum_{i,\nu,\rho=1}^{4} e_t e_i {}_t\lambda^\nu {}_i\lambda^\rho \left\{ \frac{\partial\, {}^i\lambda_\nu}{\partial x_\rho} - \frac{\partial\, {}^i\lambda_\rho}{\partial x_\nu} \right\} \\ &= \sum_{\nu,\rho=1}^{4} e_t {}_t\lambda^\nu \chi_\nu \qquad [\text{by } (9)] \\ &= \chi^*_t. \end{aligned}\right\} \quad . \quad (12)$$

Now Prof. Levi-Civita calls the lattice-vector

$$c^*_t = \sum_{i=1}^{4} e_i \gamma_{iti}$$

the "average curvature of the congruences orthogonal to the tth," *i.e.*, it is the sum of the projections on the direction "t" of the vectors representing the geodesic curvatures of the lines of the three other congruences normal to the tth.

Hence, since $e_t c^*_t = \chi^*$, it follows from (11) that, for the field (1), *the lattice tensor ϕ^*_t corresponding to the electromagnetic potential tensor ϕ_μ is proportional to the average curvature of the congruences.*

In conclusion, I should like to thank Prof. E. T. Whittaker, F.R.S., of Edinburgh University, who was good enough to communicate this paper.

CVII. *Investigations on the Effect of Crystalline Structure on Magnetic Susceptibilities by a New Magnetic Balance based on the Principle of Interference of Light.* *By* Prof. S. S. Bhatnagar, *D.Sc.* (*Lond.*), *and* R. N. Mathur, *M.Sc.*[*]

THE influence of crystalline structure on magnetic susceptibilities has been considerably investigated. Curie[†] found that red phosphorus is less diamagnetic than yellow, while the diamagnetic susceptibilities of the allotropic forms of sulphur are nearly the same. Honda and Du Bois[‡] investigated the magnetic properties of a large number of elements, some of which had allotropic modifications of different crystalline structures. The method of experimentation did not differ essentially from that of Curie. The magnetic susceptibilities of various allotropic forms of phosphorus, antimony, carbon, and tin showed interesting differences. The ordinary white tetragonal variety of tin was found to be slightly paramagnetic, while grey tin was diamagnetic. Different allotropic forms of carbon gave values which differed considerably. The allotropic modifications of phosphorus and antimony also gave different values. Honda's investigation was continued by Owen[§], and he obtained different values for the diamagnetic susceptibilities of rhombic and colloidal sulphur. Oxley[||] also investigated the influence of molecular constitution on magnetic susceptibilities. According to him the relation between molecular complexity and specific diamagnetic susceptibility x_D may be written in the form

$$x_D \doteq \frac{1}{H}\Sigma n_P \Delta M_P,$$

where ΔM_P is the total diamagnetic moment produced in a complex of type P by the application of an external magnetic field H, n_P is the number of complexes of the type P per gramme, and the summation is extended over all such types. The allotropic forms of an element which possess characteristic crystalline structures will have different molecular distorsions or types of molecular complexes, and consequently different magnetic properties. Oxley (*loc. cit.*)

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[*] Communicated by the Authors.

[†] *Ann. de Chim. et Phys.* (7) v. pp. 289–405 (1895).

[‡] *Ann. der Phys.* xxxii. pp. 1027–1063 (1910); "Versl. Kon. Ak. V. Wetensch," Amsterdam, xii. p. 601 (1910).

[§] *Ann. der Phys.* xxxvii. p. 657 (1912).

[||] Phil. Trans. Roy. Soc. A, ccxiv. pp. 108–146 (1914).

also attempted to interpret these changes in magnetic properties in terms of the electron theory of magnetism.

A large number of compounds, besides the elements described above, exist in various isomeric modifications. As for example, the oxide and iodide of mercury exist in yellow and red forms, and there are differences of opinion as to whether the change in their colour is due only to a change in size of the particles or is accompanied by a change in crystalline structure as well. The magnetic susceptibilities of substances are, in general, influenced by their crystalline forms and not by the size of their particles. Wilson * points out that if specimens are reduced to powder by a grinder in the construction of which no magnetic material is used, and then tested for magnetic susceptibilities by his balance, the susceptibilities of the original specimens are obtained. It is therefore obvious that a knowledge of the magnetic properties of isomeric modifications would throw considerable light on their constitution. An attempt was therefore made to determine the magnetic susceptibilities of the red and yellow varieties of mercuric oxide on an apparatus very similar to that described by Wilson (*loc. cit.*). The substance contained in a thin small glass phial, attached to a light aluminium system, is suspended in a non-homogeneous magnetic field by a phosphor-bronze or silver strip. The force exerted by the field is balanced by the torsion of the suspension and read off from a graduated torsion head; but as the differences between the susceptibilities of isomeric modifications are very small, the apparatus was not found sensitive enough to detect them. It was therefore necessary to construct a much more sensitive balance for this investigation.

Nearly all methods commonly used for the measurement of magnetic susceptibilities of solids may be divided into two groups: (1) those in which the specimen is placed in a non-homogeneous magnetic field like Curie's and Oxley's balances, and (2) those in which the specimen is suspended in a homogeneous field as in Gouy's method; but in every case it is the displacement of the substance placed in the magnetic field that is directly or indirectly measured. In Curie's balance the movements of the torsion-rod-pointer over a scale are noted. In Oxley's balance (*loc. cit.*) the movements of a spot of light on a scale, corresponding to the displacements of the substance in the field, are observed; while in some other balances the restoring method is employed, and the amounts of torsion to be given to the suspension wire, to bring back the specimen to its original position, are measured. Now the displacement of a substance in a magnetic field is proportional to its susceptibility, and for substances whose susceptibilities are nearly equal, the displacements for their same mass will also be nearly equal, and may not be differentiated if the apparatus is not sensitive enough. And in order to know accurately the difference between the displacements of such substances, it is necessary that the method of measuring them be very sensitive to small changes. In experiments based upon the principle of interference of light, as for example, formation of Newton's rings, we know that very small changes in the system produce very great changes in the interference rings. It therefore struck us that the displacements of the substance in the magnetic field might be measured in terms of the changes in Newton's rings. A convex lens put on a glass plate gives Newton's rings, and if the plate or lens moves a little a very big change in the position of the rings takes place at once; and either the shift of the rings from their original position can be measured or an appliance can be devised to bring the rings back to their original positions. Accordingly, du Noüy's apparatus for measuring surface tensions was adapted for the purpose of a magnetic balance. Essentially, du Noüy's apparatus is a torsion balance employing a wire to which is clamped a light arm. The torsion is applied to the wire by means of a slow-motion screw, and the angle of torsion is indicated on a graduated dial. The light arm of the balance extends only on one side of the wire. It was therefore replaced by a light aluminium beam extending on both sides of it. To its one end was attached a small convex lens and to the other a small glass tube which could be put in a suitable homogeneous magnetic field. Below the lens was placed a small plane table which could be moved up and down by means of a screw, and on this table was put a plane piece of glass. Above the lens was put a piece of glass plate, inclined at an angle of 45° to reflect light from a sodium flame vertically downwards. A right-angled prism was put above the glass plate, and Newton's rings were observed by means of a microscope. The substance whose susceptibility was to be determined was put in the glass tube. On applying the magnetic field the tube moved up and down in the field, and this produced a shift in the Newton's ring system. Attempts were made to bring the rings back to their original position by applying torsion to the wire. Sometimes the shifts of the rings were also measured by a travelling microscope. The experimental difficulties were, however, so many that they rendered the method much less promising than it at first sight appeared. Attempts were therefore necessary to employ some other device. If two converging beams of light are producing interference fringes and a moving glass plate be placed in the path of one, the shifting of the fringes will depend upon the movements of the plate and can be a measure of it. Moreover, very small movements of the plate will produce very considerable shiftings of the fringes. If, therefore, instead of measuring the movements of a spot of light on a scale, as in Oxley's balance (*loc. cit.*), we measure the shift of the fringes produced by the movements of a glass plate, the apparatus will be a very sensitive one. A Rayleigh interferometer provides interference fringes as well as possesses a convenient appliance for measuring the shifting of the fringes. It was therefore adapted for this purpose. The apparatus is represented diagrammatically in figs. 1, 2, 3, and 4.

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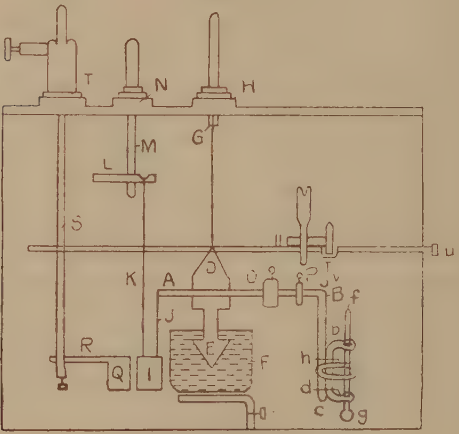
* Proc. Roy. Soc. A, xcvi. p. 442.

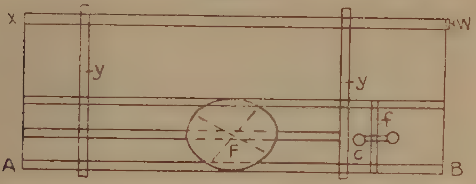
Fig. 1.



Front Elevation.

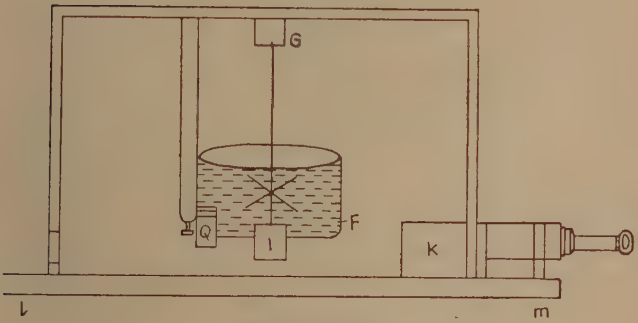
In fig. 1, ABC is a light aluminium beam bent at right angles at B. The horizontal portion of the beam is fixed to a light aluminium piece D, whose lower end has got cross vanes E. These cross vanes move in a dash pot F containing a mixture of paraffin oil and heavy mineral oil to damp the vibrations of the beam. The aluminium piece D is suspended by a fine silver strip. The other end of the strip is fixed to the rod G which, by a screw, is fixed to the torsion head H. I is a piece of optically plane parallel glass suspended by means of two silk threads J and K. The thread J is attached to the end A of the beam, while the thread K is attached to the end of rod L. The rod L passes through a hole at the end of the rod M, and can be moved forwards and backwards in it. The brass rod M is attached by a screw to the torsion head N. The system LMN is therefore a three-dimensional adjustment appliance. The end of the rod L to which the silk thread is fixed can be moved forwards and backwards by moving L, up and down by moving M up and down, and sideways by twisting M with the torsion head N. O and P are two riders placed over the beam to keep it horizontal. The rider P is much lighter than O (their respective weights being 0·08 and 0·4 gm.) and is used for fine adjustment. Q is another optically

Fig. 2.



Plan.

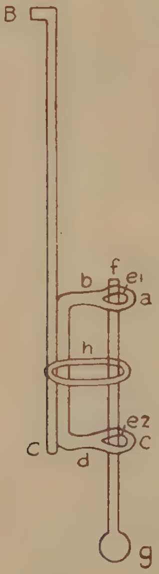
Fig. 3.



Side Elevation.

plane parallel piece of glass of the same thickness as I; it is directly attached to the end of the rod R. The system RST is exactly similar to the system LMN. This is all enclosed inside a box, having a window in front. In order to move the riders O and P over the beam AB, the arrangement of a chemical balance for moving the rider over its beam was fixed in a side of the box. U is the handle and V the hook which holds the rider. In order to rest the torsion arm AB while the phial, containing the substance under investigation, was being attached to its end C, the rod WX provided with two cranks YY was used (fig. 2). The rod WX passes through a hole in the side of the box, and can be rotated by the handle W. The arrangement for holding the phial is shown in fig. 4. BC is the end of the beam bent at right angles at B. To its end is fixed a piece of aluminium, *abcd*, bent at right angles at *b* and *d*. In the pieces *ab* and *cd* are made two V-shaped holes e_1 and e_2. The phial *gf* is put into them from below. *h* is a thin rubber band passing over the stem of the phial and the end BC of the beam. By means of this rubber band the phial is held tight to the

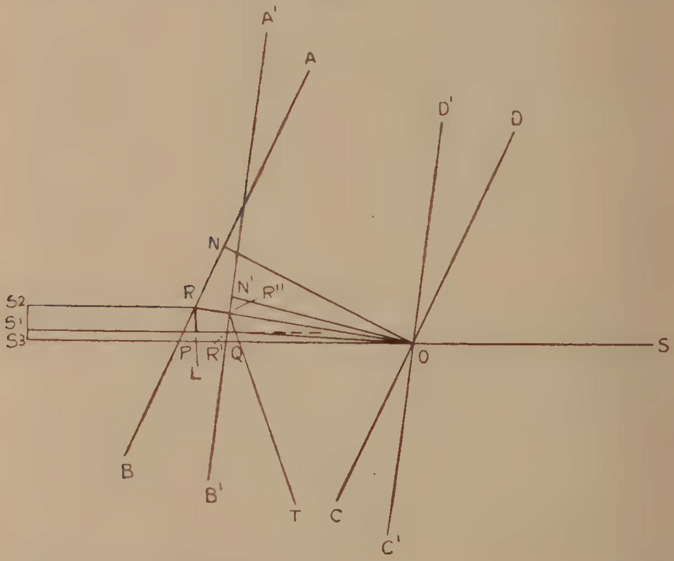
Fig. 4.



left in the V-shaped holes. At the top of the stem *f* is made a mark, and whenever the phial is placed in the holes e_1, e_2, this mark is made to coincide with another mark in the plate *ab* near the V end of the hole e_1. By this device the phial is always placed in the same position. Its displacement to the left or right is checked by the V-shaped holes e_1 and e_2 and the rubber band *h*, while its displacement sideways, or up and down, is checked by the marks on the top of the stem *f* and the plate *ab*. Any change in the position of the phial, relative to the pole-pieces of the electromagnet, can now only be due to an alteration in the position of the beam AB, and this could be detected and removed by means of the interference fringes as given afterwards. The phial *g* was placed in a suitable non-homogeneous magnetic field obtained by inclining the pole-pieces of an electromagnet at an angle. The electromagnet was also placed inside the box containing everything else, and this box was fitted over the interferometer in front of its small box containing the movable glass plate and the fixed compensating plate in such a way that the two plates I and Q were in the path of the two parallel beams of light coming from the collimator (fig. 3). *lm* is a part of the heavy base of the interferometer. I and Q are the glass plates of fig. 1 and K is the small box of the interferometer containing the glass plate moved by the micrometer screw and the fixed compensating glass plate. The parallel rays of light coming from the collimator pass through I and Q and then through the two plates in the box. The window for admitting the beams of light into the box is also covered with a piece of optically plane glass. In order to avoid vibrations of the plate I due to air currents, no holes were left open in the sides of the box. A part of the interferometer and the box were also further enclosed in a chamber, with a window, in such a way that only the eyepiece of the interferometer and its micrometer screw were out of it. By using a pointolite lamp the two sets of interference fringes were obtained, and their central black bands were made to coincide. A known weight of the substance whose susceptibility was to be determined was then put in the phial and a constant current of 1·5 amperes, taken from a set of batteries, was passed in the electromagnet. On account of the movements of the phial in the field the glass plate I turns through an angle, and the upper system of fringes shifts to one side. Their central black bands are then again made to coincide by turning the interferometer screw. The number of divisions through which the screw had to be turned are noted.

Similar readings are taken for the empty phial and phial containing a known weight of water. Let X be the force acting on the substance in the field and let θ be the angle through which the beam is turned due to it. We have now to find the change in the optical path produced by this turning of the plate I through an angle θ. In fig. 5, ABCD represents the original position of the plate and A′B′C′D′ when it has been deflected through an angle θ. SO is the incident ray and OR and OR′ the refracted rays in the two positions of the plate, and ON and ON′ the corresponding normals drawn from O. The refracted rays coming from out the plate are travelling along RS_2 and $R'S_1$. Produce SO to S_3, cutting AB and A′B′ and P and Q. Let S_1, S_2, and S_3 be in a line. From R″ draw a perpendicular R″T on S_1R' produced, and from R draw a perpendicular RL on $R'S_1$. The optical paths of the rays from S to S_1S_3 are $SO+n\,.\,OR+RS_2$ and $SO+n\,.\,OR'+R'S_1$, where n is the index of refraction of the material of the plate. The change in optical path is therefore given by

Fig. 5.



$$P=n\,.\,OR-n\,.\,OR'-R'L \qquad (RS_2=LS_1)$$
$$=n\,.\,OR-n\,.\,OR'-LT+R'T.$$

Let ϕ and ϕ' be the initial angles of incidence and refraction, and let ϕ_1 and ϕ_1' be the corresponding angles when the plate has been turned through an angle θ.

$$\therefore \qquad \mathrm{OR} = \frac{h}{\cos\phi'} \qquad (\mathrm{ON}=h \text{ is the thickness of the plate}),$$

$$\mathrm{OR}' = \frac{h}{\cos\phi_1'},$$

$$\mathrm{RR}'' = h\left[\frac{1}{\cos\phi'} - \frac{1}{\cos(\phi'-\theta)}\right],$$

$$\begin{aligned} \mathrm{LT} &= \mathrm{RR}''\cos(\phi-\phi') \\ &= h\cos(\phi-\phi')\left[\frac{1}{\cos\phi'} - \frac{1}{\cos(\phi'-\theta)}\right], \end{aligned}$$

$$\mathrm{R'N'} = h\tan\phi_1',$$

$$\mathrm{R''N'} = h\tan(\phi'-\theta),$$

$$\therefore \qquad \mathrm{R'R''} = h[\tan\phi_1' - \tan(\phi'-\theta)],$$

$$\begin{aligned} \mathrm{R'T} &= \mathrm{R'R''}\sin(\phi-\theta) \\ &= h\sin(\phi-\theta)[\tan\phi_1' - \tan(\phi'-\theta)]. \end{aligned}$$

Also
$$\sin\phi' = \frac{\sin\phi}{n},$$

$$\cos\phi' = \frac{\sqrt{n^2-\sin^2\phi}}{n},$$

$$\sin\phi_1' = \frac{\sin(\phi-\theta)}{n},$$

$$\cos\phi_1' = \frac{\sqrt{n^2-\sin^2(\phi-\theta)}}{n}.$$

Substituting these values in (1) we have for the change in optical path P

$$\begin{aligned} \mathrm{P} = h\Big\{ &\frac{n^2}{\sqrt{n^2-\sin^2\phi}} - \frac{n^2}{\sqrt{n^2-\sin^2(\phi-\theta)}} \\ &-\sin(\phi-\theta)[\tan(\phi'-\theta)-\tan\phi_1'] \\ &-\cos(\phi-\phi')\left[\frac{1}{\cos\phi'} - \frac{1}{\cos(\phi'-\theta)}\right]\Big\} \\ = h\Big\{ &\sqrt{n^2-\sin^2\phi} - \cos\phi - \sqrt{n^2-\sin^2(\phi-\theta)} \\ &+\cos\phi\cos\theta + \sin\phi\sin\theta\Big\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1) \end{aligned}$$

When θ is very small[*], $\cos\theta = 1$, and we have to a very close approximation

$$P = h\sin\theta\left\{\sin\phi - \frac{\sin 2\phi}{2\sqrt{n^2-\sin^2\phi}}\right\}. \quad . \quad . \quad (2)$$

As ϕ the initial angle of incidence remains constant, the expression inside the bracket is constant. And as h is also a constant

$$P = K\sin\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

After putting on the magnetic field, the central black bands of the two systems of interference fringes are again made to coincide. The change in optical path P is then equal in magnitude to the change in optical path produced by the movement of the interferometer plate. And the latter change is directly proportional to r', where[†]

$$r' = r - Kr^2$$

and r is the number of divisions on the drum through which the micrometer screw is turned to bring back the fringes to their original position, and K is a constant for the instrument. For our interferometer the value of K is 0·000022, and hence

$$r' = r - 0{\cdot}000022\,r^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

r' is therefore a number directly proportional to the change in the optical path.

$$\therefore \qquad P = K\sin\theta$$
$$= K_1 r',$$

where K_1 is a constant.

Now, if X is the force acting on the substance in the field,

$$X = K_3\sin\theta$$
$$= K_4 r', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

provided the deflexion of the torsion arm is small. K_3 and K_4 are constants.

Now, according to Oxley (*loc. cit.*), if the phial be placed at P with regard to the pole-pieces A and B (fig. 6), the

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[*] An estimate of the magnitude of θ is given under the discussion of possible errors (*c*).

[†] Jour. Amer. Chem. Soc. xxxvii. p. 1192 (1915).

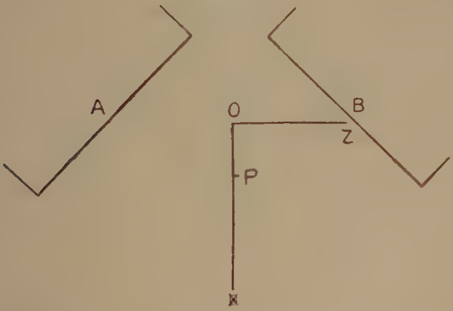
mechanical forces acting on the body of specific susceptibility x and mass M are given by

$$X = xM\left(H_x\frac{\partial H_x}{\partial x} + H_y\frac{\partial H_y}{\partial x} + H_z\frac{\partial H_z}{\partial x}\right) \quad . \quad . \quad (6)$$

along OX, with similar expressions for the forces Y and Z along OY and OZ. In practice the forces along OY and OZ are very small, and since the resistance to motion in these directions is very great the disturbance of the equilibrium of the suspended system, due to these forces, may be neglected.

Now let r_1 be the number of divisions through which the micrometer screw is turned when the phial only is placed in the field, and let r_2 and r be the similar readings when phial containing water and phial containing substance are placed in the field. Then from (5) and (6)

Fig. 6.



$$K_4(r_2-r_1) = (x_w m_w - x_a m_a)\left(H_x\frac{\partial H_x}{\partial x} + H_y\frac{\partial H_y}{\partial x} + H_z\frac{\partial H_z}{\partial x}\right), \quad . \quad . \quad . \quad (a)$$

$$K_4(r-r_1) = (xM - x_a M_a)\left(H_x\frac{\partial H_x}{\partial x} + H_y\frac{\partial H_y}{\partial x} + H_z\frac{\partial H_z}{\partial x}\right), \quad . \quad . \quad . \quad (b)$$

provided the phial is always placed in the same position relative to the pole-pieces. Here M is the mass of the substance taken, M_a that of air which fills the same volume as the substance, m_w the mass of water taken, and m_a that of air which fills the same volume as occupied by water.

In all the experiments the current was kept constant at 1·5 amperes. The factor involving the field on the right-hand side of (*a*) and (*b*) is constant, and we get

$$xM = x_a M_a + (x_w m_w - x_a m_a)\frac{r - r_1}{r_2 - r_1}.$$

The specific susceptibilities of water x_w and of air x_a are taken as $-7{\cdot}2 \times 10^{-7}$ and 210×10^{-7} respectively.

Discussion of Possible Errors.

(*a*) Change in the position of the phial relative to the pole-pieces.—While taking the readings for the empty phial, phial and water, and phial and substance, it is necessary that the phial be placed always in the same position relative to the pole-pieces. As given before, the phial can always be placed in the same position relative to the beam by means of the two V-shaped holes, rubber band, and marks on the top of the stem of the phial and aluminium plate. Any change in its position relative to the pole-pieces could then only be due to a change in the position of the beam, and this could at once be detected by the shifting of the interference fringes. A change in the horizontal position of the beam takes place on account of the varying weights of the contents of the phial. This produces a shift of the interference fringes, and the riders O and P are adjusted to bring them back to their original position. We believe that this is a much more accurate method of bringing the phial always to the same position than those used by others. Slightest changes in the weights of the contents of the phial or very small movements of the rider P over the beam produce appreciable shift of the fringes.

(*b*) Correction due to dissymmetry of phial.—The phial was as nearly spherical as possible. Moreover our measurements are differential ones, and if the phial is placed always in the same position no appreciable error can be introduced from this source.

(*c*) Error due to the assumption in deducing equation (2) that θ is so small that $\cos\theta$ is unity.—In the interferometer used the micrometer screw presses against a steel block at the end of an eight-inch lever. Further, the drum on the screw is divided into 100 equal divisions and the pitch of the screw is 1/2 mm. A rotation corresponding to one division of the drum therefore moves the end of the lever through 0·005 mm., and hence turns the compensating plate through an angle of 5 seconds. A rotation corresponding to 600 divisions, which is the maximum number of divisions measured in this investigation, will therefore move the plate through 50 mts. Now the plate I is about five times thicker than the interferometer plate. In order to produce the same change in optical path it will therefore only have to move through about 10 mts., and the value of the cosine of this small angle is always taken as unity. The magnitude of θ can also be calculated from equation (1) if we know P. Now, it can readily be shown that for light of wave-length λ the displacement of the central black fringe, measured in fringes, follows the simple relation $N = \frac{P}{\lambda}$, where P is the change in optical path and N is the number of fringes. In the present measurements N never exceeds 10, and taking for λ the wave-length of yellow light, P is of the order $5{\cdot}5 \times 10^{-4}$; and from equation (1), taking the maximum value of ϕ to be 10°, the value of θ comes to be of the same order as before, namely 10 mts.

(*d*) The phial used was slightly paramagnetic. Any variation in temperature during the time readings were being taken will therefore affect the results. But a thermometer placed inside the box practically showed no change in temperature during the interval when the readings for the phial, phial with water, and phial with the substance were being taken.

Experimental Results.

The substances investigated were always prepared as magnetically pure as possible. Rhombic sulphur was prepared by crystallizing Merck's extra pure sulphur from carbon disulphide. Monoclinic sulphur was prepared in the usual way from rhombic sulphur. In order to further test their purity, their melting-points and specific gravities were also determined, as given in the table below.

Substance.	Melting-point.	Melting-point usually given in books of reference.	Specific gravity.	Specific gravity usually given in books of reference.
Rhombic sulphur.	114° C.	115° C.	2·01	2·03
		111–115° C.		
Monoclinic sulphur.	118° C.	117·4° C. (Gernez)	1·981	1·982
		120° C. (Brodie)		1·958 (Deville)

The yellow and red modifications of mercuric iodide were obtained as follows :—Yellow mercuric iodide was prepared by a method described by Gernez *. Pure red iodide was heated in a long tube. By cooling the liquid and condensing the vapour on the cool sides of the tube the yellow variety was obtained. This easily remained stable for about a day, when it changed into red. In doing the actual experiment the yellow variety was first put in the phial and readings taken. The yellow variety was then left in the phial for a day, when it changed into red and readings were again taken. The results are shown in the table below. r, r_2, and r_1 are the number of divisions on the drum of the micrometer screw after making the correction required by equation (4).

Substances.	r.	r_2.	r_1.	$-\chi_m \times 10^6$.
Rhombic sulphur …………	388·2	339·9	531·6	0·487
Monoclinic sulphur ………	395·5	339·9	531·6	0·462
Mercuric iodide yellow……	291·6	204·0	345·5	0·272
Mercuric iodide red ………	291·6	204·0	345·5	0·272

Attempts were also made to determine the magnetic susceptibility of plastic sulphur. This variety of sulphur is usually prepared by pouring molten sulphur into water. But as it was necessary for our purpose that the specimen be absolutely free from water, it was prepared by pouring molten sulphur into a vessel cooled in ice. A small amount of plastic sulphur could be obtained in this way, but it remained stable only for a very short time. No definite readings could therefore be obtained for it, but the trend of readings showed that it is less diamagnetic than rhombic sulphur.

Discussion of Results.

According to Owen (*loc. cit.*) the diamagnetic susceptibility of rhombic sulphur is $-0·485 \times 10^{-6}$, and our result is in excellent agreement with his. On account of a change in the crystalline structure it is natural to think that the susceptibility of monoclinic sulphur will be different from that of rhombic, and we find that it is a little less. Again, although no definite results could be obtained the susceptibility of plastic sulphur is less than that of the rhombic form. Foex and Royer † have determined the values of the diamagnetic susceptibilities of some substances which pass into the nematic state, and they have interpreted the results in terms of diamagnetic orientation. According to them the susceptibility of para azoxy-anisol decreases suddenly by about 17 per cent. when it passes into the nematic state at 116° C. Our results for plastic sulphur therefore seem to be in line with the view of Foex and Royer. As for mercuric iodide, there is difference of opinion as to whether the red and yellow modifications have got the same or different crystalline structures. According to Luczizky [*] the red iodide crystallizes in tetragonal prisms and pyramids. According to Gernez [†], on cooling the liquid iodide or condensing the vapour, the yellow modification is obtained in rhombic prisms. But according to A. Smits [‡], observations made with large crystals of yellow iodide show that the gradual development of the orange colour with rise of temperature is not accompanied by any change in crystalline form. This fact points to the formation of mixed rhombic crystals containing both yellow and red modifications. They are, according to Smits, apparently two isomeric forms of mercuric iodide (α and β) ; the red and yellow modifications being mixed crystals containing the two forms in different proportions. According to all that has been said before a change in crystalline structure must be accompanied by a change in susceptibility. With our sensitive balance [§] even very small changes in susceptibility can be detected. It therefore appears that magnetic data support Smits' views.

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* *Compt. Rend.* cxxviii. p. 1516 (1899); *Compt. Rend.* cxlviii. p. 1015 (1909).

† "Le Diamagnetisme des Substances nématiques," *C. R.* clxxx. p. 1912 (1925); *Jour. de Phys. Bull.* ccxix. p. 94 (1925).

Further work on the magnetic susceptibilities of the other allotropic forms of sulphur and various modifications of mercuric oxides, sulphides, etc., is in progress and will be shortly communicated. Some substances are also being crystallized from different solvents, when they come out with different crystalline structures, and their susceptibilities are being determined.

Finally, we wish to express our thanks to Principal Hem Raj and Mr. K. N. Mathur.

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[*] *Zeit. Sch. Kryst. Min.* xlvi. p. 297 (1909).

[†] *Compt. Rend.* cxxviii. p. 1516 (1899).

[‡] *Proc. K. Akad. Wetensch. Amsterdam*, xix. p. 703 (1917).

[§] A full account of the sensitivity of the apparatus is given in an extension of this paper shortly to be communicated.

CVIII. *The Thermal Conductivity of a Single Crystal of Bismuth in a Transverse Magnetic Field.* *By* G. W. C. Kaye, *O.B.E., M.A., D.Sc., and* W. F. Higgins, *M.Sc., Physics Department, the National Physical Laboratory, Teddington, Middlesex* *.

THE fact that the thermal conductivity of bismuth in crystalline aggregate is decreased in the presence of a magnetic field was first observed independently in 1887 by Righi † and Leduc ‡. Subsequent investigations by von Ettingshausen §, van Everdingen ‖, and Blyth ¶ confirmed the sign of the change, though their results are not in good agreement. Lownds**, in 1902, examined single crystals of bismuth by the melting-wax method of de Sénarmont ††, and so obtained the effect produced by a field of about 5000 gauss on the ratio of the conductivities parallel and perpendicular to the trigonal axis. His specimens were very small, however, and approximate values only were possible.

It appeared that there was scope for a precise investigation of the effect of a transverse magnetic field on the thermal conductivity of single crystal specimens of bismuth, and the present investigation was undertaken. A "plate" type of apparatus was used similar in design to that recently employed by the authors for the thermal conductivity of solid and liquid sulphur ‡‡, with the exception that the cold block was cooled by a circulation of water instead of being air-cooled. The bismuth crystal, cut in the form of a disk 25 mm. in diameter and 2 mm thick, was sandwiched between the horizontal faces of the hot and cold blocks, the hot block being uppermost. Good thermal contact was effected by using optically flat surfaces, glycerine contact films, and a small load. Above the hot block was a "guard plate" to prevent loss of heat in the upward direction.

The transverse magnetic field was provided by an electromagnet, with pole-pieces measuring 10 cm. by 8·4 cm. The size of the conductivity apparatus necessitated a minimum gap of 4 cm. between the pole-pieces, which permitted uniform fields up to about 11,000 gauss to be attained.

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* Communicated by the Authors.

† Righi, *Mem. Acad. Linc.* (4) iv. p. 433 (1887).

‡ Leduc, *Comptes Rendus*, civ. p. 1783 (1887).

§ von Ettingshausen, Wied. *Ann.* xxxiii. p. 129 (1888).

‖ van Everdingen, Comm. Phys. Lab. Lieden, xlii. p. 4 (1898).

¶ Blyth, Phil. Mag. (6) v. p. 529 (1903).

** Lownds, *Ann. d. Physik*, ix. 3, p. 677 (1902).

†† de Sénarmont, *Comptes Rendus*, xxv. pp. 459, 707 (1847).

‡‡ Kaye and Higgins, Roy. Soc. Proc. A, cxxii. p. 633 (1929).

The change in thermal conductivity was measured for the following orientations of the crystal specimen. In each case the heat-flow was perpendicular to the magnetic field.

(*a*) Heat-flow and magnetic field both perpendicular to the trigonal axis.

(*b*) Heat-flow perpendicular to the trigonal axis; magnetic field parallel to the trigonal axis.

(*c*) Heat-flow parallel to the trigonal axis; magnetic field perpendicular to the trigonal axis.

In the case of specimens cut for investigating the heat-flow perpendicular to the trigonal axis, the value of the conductivity obtained in the absence of a magnetic field agreed closely with that found by Kaye and Roberts* in 1923 for much smaller specimens. The corresponding result for heat-flow parallel to the trigonal axis yielded, however, a figure about 18 per cent. less than the 1923 values. This low figure would be explained by the presence of fissures parallel to the principle cleavage plane (normal to the trigonal axis), an effect which has been observed by other workers using large single crystals of bismuth. It would appear that the constricting effect of the glass mould during the cooling and formation of the crystal may set up strains in the specimen which are relieved by slipping along the cleavage plane. Again, the preparation of the test specimen necessitated a certain amount of mechanical working, and strains set up during cutting and grinding operations might conceivably give rise to cracks along the cleavage planes. Such discontinuities, while having no effect on the thermal resistance parallel to the cleavage planes, might effect an appreciable increase at right-angles to them. In this connexion it may be mentioned that a twenty-fold increase of load (up to 7·5 kilogram per sq. cm.) on the specimen during test caused an increase in conductivity of 2 per cent and a permanent increase of about 1 per cent when the extra load was removed.

Figs. 1 and 2 show the change in conductivity produced by transverse fields up to 11,000 gauss. The accuracy of measurement is within $\pm\frac{1}{2}$ per cent. In the case of heat-flow parallel to the trigonal axis the graph includes results for a second specimen and for the two together.

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* Kaye and Roberts, Roy. Soc. Proc. A, civ. p. 98 (1923).

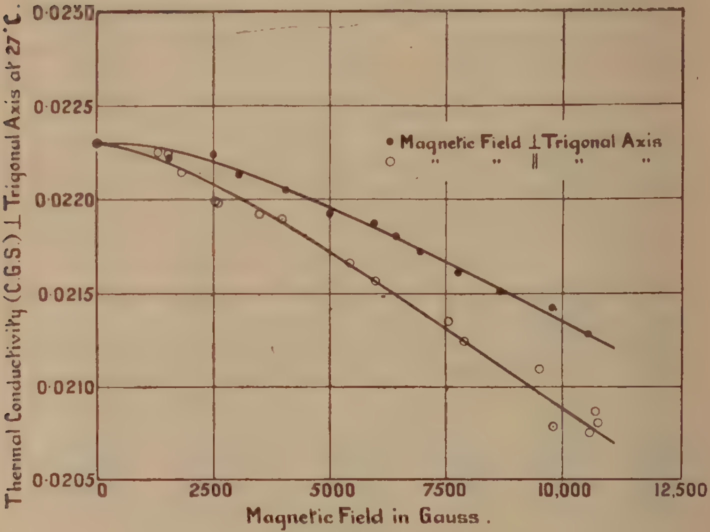

Fig. 1.—Heat-flow ⊥ Trigonal Axis.

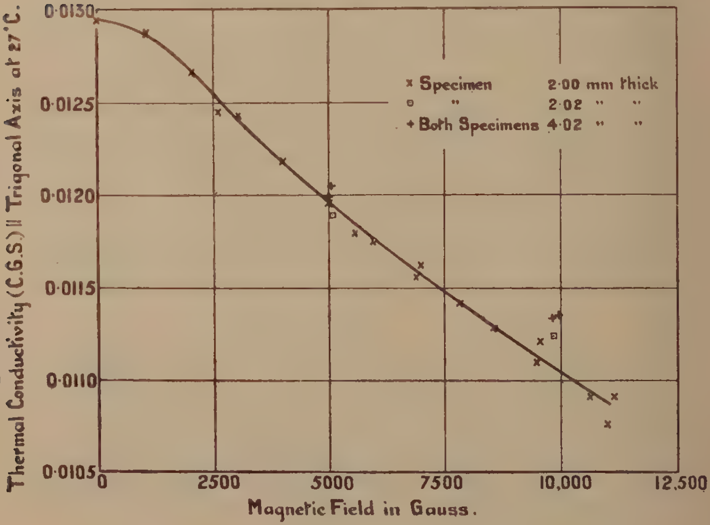

Fig. 2.—Heat-flow ∥ Trigonal Axis.

The following are the mean changes in conductivity at 27° C. for the specimens examined to date :—

Direction of heat-flow.	Direction of magnetic field.	Percentage decrease in thermal conductivity in field of 11,000 gauss.
⊥ trigonal axis	⊥ trigonal axis	4·9 %
⊥ ,, ,,	‖ ,, ,,	7·3 ,,
‖ ,, ,,	⊥ ,, ,,	16·0 ,,

The work is being continued with certain modifications and greater magnetic fields.

We are again much indebted to Mr. D. E. A. Jones for his very competent assistance.

CIX. *The Rate of Molecular Collisions in Liquid Systems.*

By Maurice Jowett, *Ph.D., B.Sc.**

THE rate of molecular collisions in liquid systems is of interest in chemical kinetics, since if the measurable process in a chemical reaction is bimolecular its rate is proportional, other things being equal, to the frequency with which the chemical species concerned collide with one another.

While the rate of molecular collisions in dilute gaseous systems has been satisfactorily treated, collision rates in liquid systems do not appear to have received much serious consideration. Thus, Christiansen (1) considers that the formulæ for collisions in gases may be applied to liquids in point of order of magnitude and in respect of their temperature coefficient. Tolman (2) regards the same formulæ as giving upper limits to the number of collisions between solute molecules in a solution.

Various chemists in discussing chemical kinetics have put forward views concerning the effect of the viscosity of the system on the collision rates between solute molecules in liquids. Thus, Moran and Lewis (3) regarded increased viscosity as hindering collisions, while Scatchard (4) regarded it as being without effect.

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* Communicated by Prof. W. C. M. Lewis, F.R.S.

In considering the subject from a physical point of view, it must be remembered that there can be no great difference between the behaviour of solute molecules and solvent molecules. If the rate of collisions between solvent molecules and solute molecules is affected in one direction by a change in the medium, then the rate of collisions between different types of solute molecules must be affected in the same direction. It can now be shown very simply that increase in viscosity is a favouring influence for collisions. Admittedly, an increase in viscosity slows down the rate of diffusion of solute molecules. Now, on the kinetic theory of diffusion, the diffusion coefficient of a substance is given approximately by the relation

$$\mathrm{D} = \tfrac{1}{3}\lambda u,$$

where λ is the mean free path of the molecule, and u is its equipartition velocity, this latter quantity being dependent only on the temperature. If therefore the viscosity of the medium be increased by any means at constant temperature, and consequently the diffusion coefficients of dissolved substances are decreased, it follows that the mean free paths of the molecules of the solutes are likewise decreased. The mean free paths being decreased, and the speed of the molecules being unchanged, the number of collisions undergone per second by these molecules must have increased.

A difficulty in appreciating this argument has perhaps been due to an incorrect appreciation of the meaning of Smoluchowski's formula (5) for the rate of rapid coagulation of colloidal particles. This may be applied to the calculation of a special type of collision rate between molecules in liquids, but not to the rate of continuous collisions.

Smoluchowski obtains the expression

$$\mathrm{J}\,dt = 4\pi(\mathrm{D}_1+\mathrm{D}_2)\nu_1\nu_2(r_1+r_2)\,dt$$

for the rate at which two types of particles, none of them initially in contact, come into contact with each other for the first time. In this way he obtains a quantity analogous to a collision rate which is of value when we do not require to take into account collisions subsequent to the first collision which two particles may undergo. The particles are regarded as diffusing into contact, and their subsequent history is not of interest for Smoluchowski, since in the case he considers they do not persist as such after first coming into contact. If they do persist, however, it is evident that after coming into contact they may undergo a number of mutual collisions before parting company. With these subsequent collisions Smoluchowski's formula is not concerned.

It is the continuous collision rate of molecules which is of interest to us, since in measurable chemical reactions in liquids only a small fraction of the total number of collisions between the two reactant chemical species concerned leads to chemical change.

An attempt has been made by Norrish and Smith (6) to calculate the rate of collisions between solute molecules in liquids by the use of the formula for collisions in gases modified to allow for the space occupied by solvent molecules. These authors suppose the rate of collision between two types of molecules to be given by the collision rate calculated from gas theory multiplied by a factor $(V/V-s)^2$, V being the volume of the system, and s the actual volume occupied by molecules themselves. The quantity $V/V-s$ is regarded as a free-space term, but this assumption is quite arbitrary. In the deduction of van der Waals's equation it is shown that the "free space" in a dilute gaseous system is equal to the total space less four times the volumes of the molecules, when collisions with a boundary are being considered. The factor will be less than four when the system is no longer dilute, since spheres of twice the molecular radius drawn round the molecules will intersect to a large extent. There is, however, no reason to suppose that the factor can become unity. Apart from this, however, the correction factor of Norrish and Smith is quite empirical, since the free-space term should not be squared. Let us for convenience replace $V-s/V$ by v_F: then the gaseous rate must be divided by v_F, not v_F^2, in order to obtain the collision rate in a liquid, since the average volume swept out by a molecule between two successive collisions is reduced from unity to v_F, not to v_F^2.

The number of collisions taking place in unit time between a single molecule of species 1 and all molecules of species 2 in a liquid system may be represented by the equation

$$ {}_1Z_2 = \frac{1}{v_{F_{12}}} . 2\nu_2 S_{12}^2 \sqrt{2\pi RT(1/M_1+1/M_2)}, \quad . \quad . \qquad (1) $$

which relates the collision rate in a liquid with that in a gas by means of a "free-space term" $v_{F_{12}}$ which has yet to be determined. It cannot be assumed *a priori* that in a liquid system containing several species of molecules the free-space term will be the same for all the types of collisions, that is, we cannot assume that

$$ v_{F_{12}} = v_{F_{13}} = v_{F_{23}} = \ldots . $$

From a purely steric point of view, for instance, regarding a liquid as an assembly of elastic spheres, fairly closely packed, we might not unreasonably suggest that a small molecule could penetrate, without collision, interspaces that the centre of a large molecule could enter only after collisions.

Kinetic Theory of Diffusion in Liquids.

An attempt may be made to evaluate v_F through the kinetic theory of diffusion applied to liquids.

The interdiffusion in a liquid system containing two kinds of molecules may be treated analogously to interdiffusion in the gaseous state. Jeans⁽⁷⁾ denotes by Γ_1 the rate of increase per unit time and area of the number of molecules of the first kind on the positive side of a plane $z=z_0$, and derives the equation

$$\Gamma_1\nu_2-\Gamma_2\nu_1=\tfrac{1}{3}\nu_1\lambda_2\bar{c}_2\frac{\partial\nu_2}{\partial z}-\tfrac{1}{3}\nu_2\lambda_1\bar{c}_1\frac{\partial\nu_1}{\partial z},$$

where ν refers to the number of molecules per c.c., λ to their free path, and $\bar{c}$ to their mean velocity.

Introducing the conditions appropriate to the liquid state, and assuming that V_1 and V_2, defined as partial molecular volumes (in the sense of other partial molecular or molar quantities), do not vary with the composition of the system, we have

$$V_1\nu_1+V_2\nu_2=1.$$

$$V_1\frac{\partial\nu_1}{\partial z}+V_2\frac{\partial\nu_2}{\partial z}=0.$$

$$\Gamma_1V_1+\Gamma_2V_2=0.$$

Combining the above four equations, we derive

$$-\Gamma_1=\frac{1}{3}\frac{\partial\nu_1}{\partial z}(V_1\nu_1\lambda_2c_2+V_2\nu_2\lambda_1\bar{c}_1),$$

whence

$$D_{12}=\tfrac{1}{3}(V_1\nu_1\lambda_2c_2+V_2\nu_2\lambda_1c_1), \quad . \quad . \quad . \quad . \quad (2)$$

where D_{12} is the coefficient of interdiffusion for the system (usually called the diffusion coefficient of the more dilute chemical species). For the special case of a dilute solution (of 1 in 2) we may take $\nu_1=0$ and find

$$D=\tfrac{1}{3}\lambda_1\bar{c}_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This relation is the same as that found for self-diffusion in gases, and was deduced by Riecke $^{(8)}$ in another manner for diffusion in a dilute solution.

As is shown by Jeans $^{(7)}$, if we consider the molecules to be elastic spheres, and allow for the tendency of velocity to persist after a collision, the above relation becomes

$$D=\frac{1{\cdot}051}{3(1-\theta_1)}\lambda_1\bar{c}_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where θ_1 is the average persistence of velocity of the solute molecule considered, a quantity taken as dependent only on the relative masses of the colliding molecules, and increasing towards unity when the molecule considered is heavy compared with the molecules with which it collides *. In making use of the above expression we are assuming that the molecular force fields are sufficiently uniform for their effects to be neglected, and that ternary collisions do not occur. Equation (4) will be applicable only approximately, and in any case only in dilute solutions.

With the limitations mentioned, the total number of collisions undergone per second by a solute molecule of species 1—these collisions being mainly with solvent molecules of species S—will then be

$${}_1Z_S=\bar{c}_1/\lambda_1.$$

or

$${}_1Z_S=\frac{1{\cdot}051}{3(1-\theta_1)}\cdot\frac{\bar{c}_1^{\,2}}{D_{1S}},$$

or

$${}_1Z_S=\frac{8\times 1{\cdot}051}{3\pi(1-\theta_1)}\cdot\frac{RT}{M_1D_{1S}}.$$

Hence

$${}_1Z_S=\frac{0{\cdot}892}{1-\theta_1}\cdot\frac{RT}{M_1D_{1S}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation allows us to calculate the total collision rate of a molecule in a dilute solution, when we know its diffusion coefficient in the solution, and also the molecular weights of the solute and solvent molecules, the latter weight being required to evaluate θ_1. The existence of an unknown degree of solvation of solutes and of polymerization of solvents may, of course, make our results of doubtful value.

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* The value of θ_1 is not very different from that of the ratio M_1/M_1+M_2.

Calculation of Collision Quantities in Aqueous Solutions.

By the use of equations (1) and (5) we shall now calculate values of ${}_1Z_S$, λ_1, and $v_{F_{1S}}$ for various substances in dilute aqueous solution at 18° C.

The diffusion data used have been taken from the 'International Critical Tables'⁽⁹⁾. The values used, with the exception of that for hydrogen, are considered to have a probable error of less than 7 per cent. When the measurements were made at a slightly different temperature, values for 18° C. have been obtained with the aid of the Sutherland-Einstein equation :

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}.$$

Values of θ_1 have been calculated by the methods given by Jeans⁽⁷⁾, only approximate values being required and obtained. It was found useful, after some values had been calculated, to obtain the remainder graphically, plotting $\left(\frac{M_1}{M_1+M_S} - \theta_1\right)$ against $\frac{M_1}{M_1+M_S}$. For the purpose of calculating θ_1 and other quantities it has been assumed that the solute molecules are not hydrated. The water molecules have been taken to be present as dihydrol ($M_S=36$). Over the large range of molecular weights in Table I., $(1-\theta_1)$ varies very widely, and the use of the concept of persistence of velocity, as calculated on the basis of elastic collisions, has therefore a very large effect on the nature of the results obtained for ${}_1Z_S$ and $v_{F_{1S}}$.

In calculating $v_{F_{1S}}$ equation (1) is used, which involves the molecular radii. For the calculation of these no exact method is available. As it is desirable that the same basis should be used for obtaining all the values in the table, a method of general applicability has been found in the assumption that at low temperatures the molecules, which are taken to be spherical, are tightly packed (occupying 74 per cent. of the space). The radii are then obtained from the formula

$$r = 6{\cdot}63 \times 10^{-9}.(Mv_0)^{1/3}, \quad . \quad . \quad . \quad . \quad (6)$$

in which v_0 is the volume of 1 gram of the substance. The density data employed for hydrogen, oxygen, and carbon dioxide refer to these substances in the solid state at the lowest temperature for which measurements are available. For the remainder of the substances the density data used

TABLE I.—Collision Quantities for Substances dissolved in Water at 18° C.

Substance.	M_1.	θ_1.	$D_{18} \times 10^5$.	$r_1 \times 10^8$.	${}_1Z_S \times 10^{-13}$	$\lambda_1 \times 10^{10}$.	$v_{F_{18}}$.
Hydrogen	2	0·050	4·9	1·97	23·0	7·6	0·071
Oxygen	32	·376	1·98	1·87	5·5	8·0	·096
Methyl alcohol	32	·376	1·40	2·28	7·7	5·7	·082
Acetonitrile	41	·437	1·38	2·48	6·8	5·7	·096
Carbon dioxide	44	·454	1·71	1·99	5·3	7·1	·098
Ethyl alcohol	46	·465	1·09	2·57	8·0	4·5	·082
Allyl alcohol	58	·520	0·98	2·70	7·9	4·1	·084
Acetamide	59	·524	0·98	2·46	7·8	4·1	·076
Urea	60	·528	1·12	2·36	6·8	4·7	·064
Propyl alcohol	60	·528	0·95	2·79	8·0	4·0	·085
Butyl alcohol	74	·580	0·84	2·99	8·3	3·5	·086
Pyridine	79	·596	0·63	2·87	10·7	2·6	·063
Isoamyl alcohol	88	·623	0·75	3·15	8·7	3·0	·085
Glycerol	92	·635	0·78	2·77	8·2	3·1	·077
Hydroquinone	110	·678	0·73	2·89	8·3	2·8	·078
Resorcinol	110	·678	0·72	2·92	8·5	2·8	·078
Chlorhydrin	110·5	·679	0·83	2·90	7·3	3·2	·089
O. hydroxy benzyl alcohol	124	·705	0·68	3·15	8·7	2·6	·078
Pyrogallol	126	·708	0·61	2·93	9·6	2·3	·067
Dichlorhydrin	129	·714	0·82	3·03	7·1	3·1	·094
Arabinose	150	·745	0·65	3·01	8·7	2·3	·076
Glucose	180	·781	0·57	3·24	9·6	1·9	·073
Mannitol	182	·783	0·55	3·27	9·9	1·8	·072
Lactose	342	·873	0·41	4·03	12·1	1·1	·073
Maltose	342	·873	0·40	4·02	12·4	1·1	·071
Sucrose	342	·873	0·41	3·98	12·1	1.1	·072
Raffinose	504	·911	0·34	4·65	14·2	0·8	·074

refer to temperatures in the neighbourhood of 20° C., some of the substances being solid and others liquid. At this temperature the packing is hardly likely to be close, and therefore the radii obtained may be too large; on the other hand, if the molecules are not spherical, the assumption of sphericity gives too low a value for the radius, and the two sources of error may to some extent cancel each other.

Since water has been taken as dihydrol, ν_S has the value $1{\cdot}68 . 10^{22}$, and equation (1) takes the form

$$_1Z_S = \frac{1}{v_{F_{1S}}} . 1{\cdot}31 \times 10^{28} . S_{1S}^2 \sqrt{\frac{1}{M_1} + \frac{1}{36}} \quad . \quad . \quad . \quad (7)$$

In this S_{1S} is, of course, the sum of the radius of the molecule of species 1 and that of the molecule H_4O_2, which has been calculated as $2{\cdot}19 . 10^{-8}$ by equation (6), taking v_0 to be 1 c.c.

It is evident from Table I. that the collision rate reaches its highest values when the molecular velocity is high or when the molecular radius is large, and passes through a flat minimum for molecules of medium weight. The collision rate ranges from about 5 to 20×10^{13}, and is hence about 10^4 times as great as in a gas at ordinary temperatures and pressures, due mainly to the higher total molecular concentration (10^3 times as great) in a liquid.

The mean free path decreases as the molecular size increases. This is, of course, due to the definition of free path used, a free path of a large molecule being regarded as terminated by a single collision with a small one, although the molecule continues its motion almost unaffected. The free path ranges from about 8 to 1×10^{-10} cm., about 10^{-4} times the value in a gas.

The free-space term $v_{F_{1S}}$ is, roughly, constant, its mean value being 0·080, and the average deviation from the mean just under 10 per cent. This deviation is of the order that would be expected in view of the probable errors in the diffusion data and molecular radii. It is thus probable that $v_{F_{1S}}$ is really a definitely constant quantity of about 0·080. That is, taking water as dihydrol, the collision rates calculated at 18° C. are about 12·5 times as great as those calculated from the formula for collisions in dilute gases.

Since v_F is a constant when the collisions considered are between water molecules on the one hand, and many and varied types of solute molecules on the other hand, it is only reasonable to suppose that equation (1) will be applicable to collisions between two solute molecules in water with the same value of v_F.

The value of v_F derived holds, of course, only for one liquid medium at one temperature. The conclusion that v_F has a constant value for collisions between any two molecules in any one liquid medium at any one temperature may reasonably be drawn. There seems no reason to restrict the conclusion to cases where the molecules considered are in dilute solution; where one or both are present in large amounts, it must, however, be recognized that the medium is a different one than is the case when the solution is dilute.

The value of v_F, being specific for each medium, cannot be calculated by the present method without extensive diffusion data, and even if it can be obtained, the numerical value reached is to some extent dependent on the degree of polymerization assumed for the medium. Approximate methods of more general applicability will be discussed in the next section.

It should, perhaps, be emphasized that other definitions of a collision than that employed by Jeans are possible, and these would lead to different collision rates. Neighbouring molecules in a liquid must be undergoing mutual interactions quite continuously. The degree of interaction here regarded as a collision is defined by saying that it is sufficient to alter considerably the motion of the smaller molecule taking part.

Calculation of Collision Quantities in a Pure Liquid.

As it has been shown for the case of one liquid medium, namely, water, that v_F is constant for collision rates of various molecules in solution in that medium, estimation of the "free space" term v_F for collisions between like molecules in a pure liquid should also give us the value of v_F for collisions between any molecules in dilute solution in that liquid.

For the case of auto-diffusion in the pure liquid, the molecules are of equal mass; θ has the value 0·406, and equation (5) becomes

$$Z = \frac{1{\cdot}500\,\mathrm{RT}}{\mathrm{MD}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

D is obviously not a measurable quantity, and to proceed further it is necessary to evaluate it. We shall do so by assuming the validity of the Sutherland-Einstein diffusion equation, which, according to Cohen and Bruins (10), reproduces well the variation of the diffusion coefficient with temperature, but gives values of the molecular radii which are only in very moderate agreement with those derived in other ways. Hence the accuracy of the results we shall obtain is limited. Using this equation, equation (8) becomes

$$Z = \frac{9\pi\eta r N}{M}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Hence in any one liquid there is a linear relation between collision rate and transport of momentum, or viscosity. Since the two molecules concerned in a collision are of the same chemical species, equation (1) takes the form:

$$v_F Z = 16\nu r^2 \sqrt{\frac{\pi RT}{M}}.$$

If we now write ν as equal to $\frac{N}{Mv}$, where v is the volume of 1 gram of the liquid, we have

$$v_F Z = \frac{16 N r^2}{Mv} \sqrt{\frac{\pi RT}{M}},$$

which on combination with equation (9) gives

$$v_F = \frac{16r}{9\eta v} \sqrt{\frac{RT}{\pi M}}$$

or

$$v_F = 9150 \times \frac{rT^{1/2}}{\eta v M^{1/2}}. \quad . \quad . \quad . \quad . \quad (10)$$

Equation (10) can be used for evaluating v_F, or we can proceed to obtain an equation which does not explicitly contain the molecular radius.

It is for this purpose desired to replace r by a value in terms of the critical volume. According to Lorenz * the critical volume (v_c) of a substance is very nearly 3·75 times its volume at absolute zero (v_0), and if this estimate is combined with equation (6), equation (10) becomes

$$v_F = 3{\cdot}90 \times 10^{-5} . \frac{v_c^{1/3} T^{1/2}}{\eta v M^{1/6}}. \quad . \quad . \quad . \quad . \quad (11)$$

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* Quoted by Herz (11). The values of Berthelot are similar.

Equations (10) and (11) give a value of v_F which is little dependent on the extent of association which is assumed to exist in the liquid; if the degree of association is n, it can easily be seen that v_F varies proportionately only to $n^{1/6}$.

Now, Batschinski [12] has studied fully an empirical equation for viscosity,

$$\eta = \frac{c}{v-\omega},$$

in which c and ω are specific constants for each liquid. The equation reproduces very well the variation of viscosity with temperature for most liquids, excepting those usually regarded as associated. The constant ω is related to the critical volume. Batschinski showed that on the theory of mechanical similarity the term $\frac{c M^{1/2}}{T_c^{1/2} v_c^{1/3}}$ should be constant, and found that for eighteen normal liquids studied by Young it has the value $3{\cdot}58 . 10^{-6}$, with an average deviation of 3 per cent.

Combining this value with equation (11), we have

$$v_F = 1{\cdot}09 \,.\, \frac{c}{\eta v} \,.\, \left(\frac{T}{T_c}\right)^{1/2},$$

or

$$v_F = 1{\cdot}09 \,.\, \frac{v-\omega}{v} \,.\, \left(\frac{T}{T_c}\right)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Equation (12) relates Batschinski's "free-space term" with that which concerns us. The two terms are very similar, but their ratio is dependent on the temperature.

In Table II. values of v_F have been calculated from equation (12) for a few liquids, some of the numerous data analysed by Batschinski having been used. It should be remembered that the accuracy of the values of v_F, apart from the general accuracy of the diffusion theory, is limited chiefly by the agreement between values of r obtained from the Sutherland-Einstein diffusion equation and from the volume at low temperatures. The liquids are assumed not to be associated.

Evidently v_F can range in liquids at ordinary temperatures over values from about 1/20 to 1/6, though the possible range is, of course, greater.

It is perhaps of interest at this point to collect together some approximate figures showing the relative magnitudes of the various volume terms which have been discussed.

These are given in Table III., relative to the critical volume as unity.

The basis on which v_0 and the next figure are calculated has already been indicated, and the b term is calculated from

TABLE II.

Free Space in Liquids at 20° C.

Substance.	$\frac{v-\omega}{v}$.	T_c (°C.).	v_F.	$\frac{v_F\ (30°\ C.)}{v_F\ (20°\ C.)}$.
Carbon tetrachloride	0·078	283	0·062	1·160
Benzene	0·079	288·5	0·062	1·157
Chloroform	0·125	262·5	0·101	1·108
Methyl acetate	0·131	234	0·108	1·111
Hexane	0·133	235	0·110	1·107
Acetone	0·148	236	0·123	1·101
Ethyl acetate	0·152	250	0·123	1·088
Pentane	0·165	197	0·142	1·097
Ether	0·174	194	0·150	1·095

TABLE III.

Relative Magnitude of various Volume Terms.

Critical volume (v_c)	1·00
Van der Waals's b	0·77
Volume of liquid at normal boiling-point	0·37
Volume of liquid at normal freezing-point	0·34
Batschinski's ω	0·31
Volume of solid at absolute zero (v_0)	0·26–0·27
Sum of volumes of individual molecules	0·19
The "free space" term v_F	0·02–0·06

them, the value obtained being higher than those usually reached in other ways. Evidently v_F is much smaller than the *actual* free space in a liquid, that is, much less than the difference between the total volume and the sum of the volumes of the individual molecules. To obtain v_F we have to subtract from the total volume about 1·6 times the volume of the molecules; this factor may be compared with the Norrish and Smith factor 1 and the van der Waals factor 4.

Collision Rate as a Function of Temperature.

It has been shown that the collision rate in liquids is considerably greater than that calculated from gas theory. As the temperature rises the general behaviour of a liquid deviates less from that of a gas; this is true also of collision rates. In other words, with rise of temperature the value of v_F rises towards unity.

It can readily be shown from equations already given (*e. g.* equations (9) and (10)) that, provided the degree of association of the medium does not vary rapidly with temperature, it is very nearly true to write:

$$\frac{d\log v_F}{dT}=\frac{1}{2T}-\frac{d\log\eta}{dT} \quad . \quad . \quad . \quad . \quad . \quad *(13)$$

and

$$\frac{d\log Z}{dT}=\frac{d\log\eta}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Equation (14) states that the temperature coefficient of collision rates in a liquid system is the same as that of viscosity, for thermal expansion will alter concentrations to an extent usually negligible. (It is naturally assumed that the concentrations of the chemical species considered do not for any other reason change with temperature.)

The temperature coefficient of collision rates is therefore negative, and continues to be so at least until the critical temperature is reached.

For liquids under ordinary conditions the decrease in collision rates is quite considerable for a rise in temperature of 10° C.; whereas $\sqrt{T}$ increases by less than 2 per cent., v_F increases by 10–15 per cent., as shown in Table II.

Previously it has been the custom in calculating temperature coefficients of velocities of bimolecular reactions in liquids to neglect the temperature coefficients of collision rates or to regard them as being the same as in gases.

It now appears that this procedure will lead to erroneous values for energies of activation of reactions, where the

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* At two temperatures T_2 and T_1, we have

$$\frac{v_{F_2}}{v_{F_1}}=\frac{\eta_1}{\eta_2}\sqrt{\frac{T_2}{T_1}}.$$

process of which the velocity is measured is actually bimolecular.

The effect of introducing the temperature coefficients of collision rates as calculated here will be to increase the energies of activation derived by some 1500–3000 calories. Such a correction is by no means negligible.

Summary.

An attempt has been made to calculate collision rates in liquids by applying to liquids the kinetic theory of diffusion, with the use of the concept of persistence of velocity. It is found that the collision rates are higher than those calculated by gas formulæ, and higher by a multiple which is probably a constant for each liquid medium at any one temperature. Approximate formulæ are given for the general calculation of this multiple, which is of the order of 10.

The temperature coefficient of collision rates is negative and approximately equal to that of viscosity. It is pointed out that this introduces a correction into calculations of energies of activation for bimolecular reactions in liquid systems.

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CX. *Electronic Waves.*

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Summary.

In a former paper (Phil. Mag., Dec. 1928) I considered the electronic waves accompanying an electron moving uniformly in a straight line. In this paper I consider the waves in the general case, when the electron is under the action of an electric force, so that its velocity and direction of motion are changing. The point of view taken is that the distribution of the sub-electrons in the atmosphere of the electron is affected by the electric force, so that the waves are no longer moving through a uniform medium but one whose properties vary from point to point.

It is shown that in this case both the electric and magnetic forces in the electronic waves are at any point at right-angles to the path a point electron would describe under the action of the electric force. As the direction of propagation of the waves is at right-angles to both the electric and magnetic forces, the waves are always travelling along what would be the path of the point electron.

The electric force E in the electronic wave is shown to be represented to a close approximation by the expression

$$\mathrm{E} = \frac{\mathrm{A}}{q^{1/2}} \cos\left(pt - \frac{p_0}{c^2}\int q\,ds\right),$$

and the magnetic force H by

$$\mathrm{H} = \mathrm{A}' q^{1/2} \cos\left(pt - \frac{p_0}{c^2}\int q\,ds\right).$$

Here ds is an element of the path of the point electron and q the velocity which such an electron would have when it reached ds; q is not the velocity at the time t of the electron associated with the train of waves. The waves stretch out far in front of this electron, and at any point P there is a definite value of q which does not change as the electron approaches P. When the electron arrives at P its velocity is equal to q.

If the path of the point electron is not a closed curve the existence of electronic waves introduces no new condition, and any such path is a possible path for the electron with its waves. When, however, the path of the point electron is a

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* Communicated by the Author.

closed curve the conditions are different. The electric and magnetic forces must recur on a complete circuit of the curve; hence, from the expressions for E and H, if S is the perimeter of this curve,

$$\frac{p_0}{c^2}\int_0^S q\,ds = 2\pi n,$$

where n is an integer. Only curves which satisfy this condition are possible for the electron accompanied by its waves. This condition leads to the same results as those usually deduced by quantum mechanics.

When the path of the point electron is not a closed curve there is radiation of energy, unless the velocity of the electron is uniform; but when the path is a closed curve the energy in the waves moves round and round the curves, none of it gets loose, and there is no radiation. In the latter part of the paper the distribution of electric waves when an electron passes through a crystal is calculated.

IN 'Beyond the Electron' and "Electronic Waves" (Phil. Mag. vi. p. 1254 (1928)) I have supposed that the waves which have been proved to accompany a moving electron are electric waves in an atmosphere surrounding the nucleus of the electron. The atmosphere contains parts—sub-electrons—which can be set in motion by electric forces and which, when moving, produce the effects of electric currents. An atmosphere of this kind would, when light or other electric waves passed through it, behave like a dispersive medium, and have a refractive index depending on the frequency of these waves. The case which is especially important in connexion with electronic waves is when the frequency of the waves passing through the medium is much greater than the frequencies of the individual sub-electrons about their positions of equilibrium. Under these conditions the medium under the influence of electric waves behaves as if the sub-electrons were free, and the connexion between the wave-length and the phase velocity is a very significant one.

An alternating electric field in the region adjacent to the electron will produce, in addition to the usual displacement current proportional to the rate of change of the electric force, convective currents due to the motion of the sub-electrons in the electric field; the effective current is the sum of these currents. The atmosphere around the electron has a natural period of vibration as a whole, independent of that of the individual sub-electron but depending on the number of sub-electrons per unit volume of the atmosphere. When the atmosphere is oscillating in this period the convective current just balances the displacement one, the effective current vanishes, and with it the magnetic force. As the magnetic force vanishes, and with it the Poynting-vector, there is no transmission of energy and no loss of energy by radiation; the oscillations can persist indefinitely.

In my former papers I showed that when the electron is moving uniformly with velocity u parallel to the axis of x, its atmosphere is traversed by a system of electrical waves represented by

$$\mathrm{Y} = \mathrm{A}\cos\left(pt - \frac{p_0}{c^2}ux\right), \quad . \quad . \quad . \quad . \quad (1)$$

where p_0 is the natural frequency of the atmosphere of the electron and is given by the equation

$$p_0{}^2 = \mathrm{N} . c^2 \frac{e'^2}{4\pi . m'},$$

where N is the number of sub-electrons per unit volume, e' the charge, and m' the mass of a sub-electron.

$$p^2 = p_0{}^2\left(1 + \frac{u^2}{c^2}\right), \quad \text{or, more accurately,} \quad \frac{p_0{}^2}{1 - \frac{u^2}{c^2}}.$$

The waves represented by (1) have a wave-length given by

$$\frac{2\pi}{\lambda} = \frac{p_0 u}{c^2},$$

a phase velocity equal to c^2/u, and a group velocity equal to u; the group velocity is also the velocity with which energy travels through medium. Thus the energy in the wave, since it travels with the same velocity as the electron, does not get dissociated from it, and no free radiant energy arises from the motion of the electron.

The preceding results apply to an electron moving uniformly. We shall now proceed to the consideration of an electron changing its velocity under the action of an electric force.

The wave equations in the atmosphere of the electron are, if X, Y, Z are the components of the electric and α, β, γ those of the magnetic forces,

$$\left(\frac{dX}{dt}+p_0^2\int X\,dt\right)=c^2\left(\frac{d\beta}{dz}-\frac{d\gamma}{dy}\right),$$

where $$p_0^2=4\pi c^2 . Ne_1^2/m,$$

when N is the density of the sub-electrons at (x, y, z).

There are similar equations for Y and Z, and three equations of the type

$$\frac{dX}{dz}-\frac{dZ}{dx}=\frac{d\beta}{dt}.$$

If the electrical and magnetic quantities vary with the time proportionally to ϵ^{ipt}, the preceding equations may be written

$$(-p^2+p_0^2)X=c^2ip\left(\frac{d\beta}{dz}-\frac{d\gamma}{dy}\right),$$

$$\frac{dX}{dz}-\frac{dZ}{dx}=ip\beta.$$

When the atmosphere of the electron comes under the influence of an external electric force, the distribution of the sub-electrons in it may be affected, and N, their density, may vary from point to point. We assume that the action of the external force is to introduce into the expression for N, and therefore into p_0^2, a term proportional to the potential V of the external force, so that if N_0 is the value of N when the electron is free from force, N, under the action of the force, will be given by the equation

$$N=N_0\left(1+\frac{2Ve}{m_0c^2}\right),$$

where e is the charge and m_0 the mass of an electron. The value of V must be chosen so that it vanishes when the charged body which is the source of the force is at an infinite distance from the electron. We have, also, in the equations in which p_0^2 occurs, to write $p_0^2\left(1+\frac{2Ve}{m_0c^2}\right)$ in place of p_0^2; $p_0/2\pi$ is the frequency of the vibrations of the atmosphere of an electron at rest and free from electric force. We shall now apply these equations to some special cases

Electronic Waves associated with an Electron acted upon by a Uniform Electric Force.

Suppose the electric force on the electron acts parallel to x in the positive direction, and that the electron is moving in this direction. Let Y be the electric force in the electronic wave; then in the one-dimensional problem where the electrical quantities depend upon x only, the equations determining the electric waves, if the time factor is ϵ^{ipt} and if γ is the magnetic force, which will be perpendicular to x and y, are

$$\left\{-p^2+p_0^2\left(1+\frac{2\mathrm{V}e}{m_0c^2}\right)\right\}\mathrm{Y}=ipc^2\frac{d\gamma}{dx},$$

$$\frac{d\mathrm{Y}}{dx}=ip\gamma.$$

In the case of a uniform electric force F,

$$\mathrm{V}=-\mathrm{F}x,$$

and the equations give

$$c^2.\frac{d^2\mathrm{Y}}{dx^2}+\left(p^2-p_0^2\left(1-\frac{2\mathrm{F}ex}{m_0c^2}\right)\right)\mathrm{Y}=0. \quad . \quad . \quad (1)$$

Suppose a uniformly moving electron enters the field of force where $x=0$, and that u_0 is its velocity and λ_0 its wavelength; then

$$\frac{p^2-p_0^2}{c^2}=\frac{4\pi^2}{\lambda_0^2}=\frac{u_0^2p_0^2}{c^4}.$$

Equation (1) may be written in the form

$$\frac{d^2\mathrm{Y}}{dx^2}+(a+bx)\mathrm{Y}=0, \quad . \quad . \quad . \quad . \quad (2)$$

where $a=\dfrac{4\pi^2}{\lambda_0^2}$ and $a/b=l$,

where l is the distance through which the force must act to double the initial kinetic energy of the electron

$$\frac{a}{b^{2/3}}=(4\pi^2)^{1/3}\left(\frac{l}{\lambda}\right)^{2/3}.$$

Now λ for ordinary velocities of free electrons is small compared with atomic dimension, while l will be comparable with these dimensions if F is an inter-atomic force and small compared with them for forces not of this character; hence $a/b^{2/3}$ will generally be an exceedingly small quantity.

If

$$\xi = \frac{a+bx}{b^{2/3}}$$

(2) becomes

$$\frac{d^2Y}{d\xi^2} + \xi Y = 0.$$

Lommel (Gray and Mathews, 'Bessel's Functions,' p. 233) has shown that the solution of this equation is

$$Y = \sqrt{\xi} . \left(AJ_{1/3}\left(\frac{\xi^{3/2}}{\frac{3}{2}}\right) + BJ_{-1/3}\left(\frac{\xi^{3/2}}{\frac{3}{2}}\right)\right).$$

As $a/b^{3/2}$ is very large, ξ will also be very large, and we may use the form of Bessel's Functions suitable for large values of the variable. Doing this, and restoring the time-factor, we find

$$Y = \frac{A}{\xi^{1/4}} \cos\left(pt - \frac{\xi^{3/2}}{\frac{3}{2}} - \alpha\right),$$

where α is a constant. This is equivalent to

$$Y = \frac{A}{(a+bx)^{1/4}} \cos\left(pt - \frac{(a+bx)^{3/2}}{\frac{3}{2}b} - \alpha\right).$$

To get the phase velocity, we notice that if the phase remains unaltered for increments δt and δx in t and x respectively,

$$p\delta t - (a+bx)^{1/2}\delta x = 0;$$

hence the phase velocity is

$$\frac{p}{\sqrt{a+bx}}.$$

The product of the group and phase velocity is equal to c^2; hence the group velocity is $(a+bx)^{1/2}c^2/p$.

From the equations

$$a = \frac{p_0{}^2u^2}{c^4}, \qquad b = p_0{}^2\frac{2Fe}{m_0c^4};$$

$$a + bx = \frac{p_0{}^2}{c^4}\left(u^2 + \frac{2Fex}{m_0}\right)$$

$$= \frac{p_0{}^2}{c^4} V^2,$$

where V is the velocity which will be attained by the electron when it reaches x, if it starts from $x=0$ with velocity u_0.

Substituting this value, we find that the group velocity of the waves at x equal V and the phase velocity c^2/V. The amplitude of Y is proportional to $(a+bx)^{-1/4}$, *i.e.* to $\mathrm{V}^{-1/2}$. What energy there may be in the electronic waves is proportional per unit volume to Y^2, *i. e.*, to V^{-1}; the velocity of the energy is equal to V; hence the energy transmitted across unit area in unit time is constant, so that there is no accumulation of energy in the waves. Since the velocity of the energy at a point in front of the electron is greater than the velocity of the electron, energy will separate from the electron and there will be radiation. In the case of the electron in uniform motion the velocity of the energy is always the same as that of the electron, so that energy does not escape from the electron.

Consider an electron moving in the direction in which the force acts. The wave-lengths of the electronic waves and their group velocity vary from point to point in the atmosphere of the electron. The group velocity is greater in the front of the atmosphere than in the rear. We see from the preceding investigation that when any portion of the atmosphere is passing a point P fixed in space the group velocity of the electronic waves in that portion is equal to the velocity which an electronic charge would possess if it started from $x=0$ with the initial velocity of the electron and fell to P under the action of the electric force. Thus, when the electron arrives at any point the group velocity of the electronic waves in its atmosphere at that point is equal to the velocity of the electron.

We have seen that the solution of the equation

$$\frac{d^2\mathrm{Y}}{dx^2}+\mathrm{PY}=0,$$

when P is of the form $a+bx$, is approximately

$$\mathrm{Y}=\frac{1}{\mathrm{P}^{1/4}}\cos\left(\frac{\mathrm{P}^{3/2}}{\frac{3}{2}b}+\alpha\right)$$

or

$$\mathrm{Y}=\frac{1}{\mathrm{P}^{1/4}}\cos\left(\int_0^x\sqrt{\mathrm{P}}\,dx+\alpha\right).$$

This form is applicable under the conditions which hold for electronic waves when P is not limited to being a linear function, but has the more general form

$$\mathrm{P}=\frac{1}{c^2}\left(p^2-p_0{}^2-\frac{p_0{}^2\mathrm{V}e}{m_0c^2}\right),$$

where V is the potential of the forces at the place x.

For, if

$$Y=\frac{1}{P^{1/4}}\cos\left(\int\sqrt{P}\,.\,dx-\alpha\right),$$

say

$$=\frac{1}{P^{1/4}}\cos\theta,$$

then

$$\frac{d^2Y}{dx^2}=\frac{5}{16}\frac{1}{P^{9/4}}\left(\frac{dP}{dx}\right)^2\cos\theta-\frac{1}{4}\frac{1}{P^{5/4}}\cos\theta\frac{d^2P}{dx^2}-\frac{P}{P^{1/4}}\cos\theta.$$

For electronic waves the first and second terms on the right-hand side are very small compared with the third. The ratio of the first to the third term is, neglecting the numerical factor,

$$\frac{1}{P}\left(\frac{1}{P}\cdot\frac{dP}{dx}\right)^2.$$

Now

$$P=\frac{p_0^2}{c^4m}(E_0+E),$$

where E_0 is the initial energy and E the fluctuating part due to the action of the electric force,

$$\frac{1}{P}\frac{dP}{dx}=\frac{\frac{dE}{dx}}{E_0+E}.$$

Now suppose ΔE is the maximum value of the fluctuation and d the range in x between a maximum and minimum for E ; then dE/dx will be of the order $\Delta E/d$ and

$$\frac{1}{P}\left(\frac{1}{P}\frac{dP}{dx}\right)^2$$

will, since

$$\frac{p^2-p_0^2}{c^2}=\frac{4\pi^2}{\lambda_0^2},$$

be of the order

$$\frac{\lambda^2}{d^2}\left(\frac{\Delta E}{E_0+E}\right)^2,$$

where λ is the wave-length of the electronic waves. Thus, when the wave-length of the electronic waves is small compared with $d(E_0+E)/\Delta E$, the first term in (1) may be neglected in comparison with the third. Similar considerations will show that the same condition makes the second term negligible in comparison with the third.

The approximation ceases to be valid when the fluctuations in P are so great that the minimum value is but a small fraction of the maximum one.

The value

$$\frac{1}{P^{1/4}}\cos\int\sqrt{P}\,dx$$

is the asymptotic one, which, as we have seen under suitable conditions, is a close approximation. As in the case of Bessel's Functions, a still closer approximation can be got by taking as the solution

$$\frac{S_1}{P^{1/4}}\cos\int\sqrt{P}\,.\,dx+\frac{S_2}{P^{1/4}}\sin\int\sqrt{P}\,.\,dx,$$

where S_1 and S_2 are power series of the form

$$1+\Sigma a_n\xi^n;$$

where ξ is a quantity of no dimensions

$$\xi=\frac{dP}{dx}\Big/P^{3/2}$$

satisfies this condition and is small.

The argument of the harmonic term is the same in the more general expression as in the asymptotic one. In many problems on electronic waves the most important factor is the argument of the harmonic terms, and it is immaterial whether the factor by which these terms are multiplied is $1/P^{1/4}$ or a power series.

We shall now consider the general case of an electron moving in a plane under the influence of an electric force whose potential is V. If before the electron enters the field of force the components of its velocity parallel to the axes of x and y are respectively u_0 and v_0, the electric and magnetic forces in the electronic waves are proportional to

$$\cos\left(pt-\frac{p_0}{c^2}(u_0x+v_0y)\right),$$

where

$$p^2-p_0^2=\frac{u_0^2+v_0^2}{c^2}p_0^2.$$

We shall suppose that the waves are plane polarized. If the electric force is in the plane xy, the plane in which the electron moves, the magnetic force γ will be at right-angles to this plane, and all the electric and magnetic quantities can be expressed in terms of γ. If, on the other hand, the electric force Z is at right angles to this plane, they can all be expressed in terms of Z. Let us take the case when the electric force X, Y is in the plane xy.

The wave-equations are—

$$\mathrm{X}\left(ip + \frac{p_0^2}{ip}\left(1 + \frac{2\mathrm{V}e}{m_0c^2}\right)\right) = -c^2\frac{d\gamma}{dy}$$

or

$$\mathrm{X}\left(-p^2 + p_0^2\left(1 + \frac{2\mathrm{V}e}{m_0c^2}\right)\right) = -c^2ip\frac{d\gamma}{dy}$$

or

$$-\frac{\mathrm{X}p_0^2}{c^2}\left(u_0^2 + v_0^2 - \frac{2\mathrm{V}e}{m}\right) = -c^2ip\frac{d\gamma}{dy};$$

but

$$u_0^2 + v_0^2 - \frac{2\mathrm{V}e}{m} = q^2,$$

where q is the velocity which a point charge starting with the velocity u_0v_0 would attain at the point xy under the influence of a field represented by V. Hence the wave equations are

$$\left.\begin{aligned} \frac{\mathrm{X}p_0^2}{c^4}q^2 &= ip\,.\,\frac{d\gamma}{dy}, \\ \frac{\mathrm{Y}p_0^2}{c^4}q^2 &= -ip\,.\,\frac{d\gamma}{dx}, \\ \frac{d\mathrm{Y}}{dx} - \frac{d\mathrm{X}}{dy} &= ip\gamma. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The equation to determine γ is therefore

$$\frac{p_0^2}{c^4}\gamma = -\frac{d}{dx}\,.\left(\frac{1}{q^2}\frac{d\gamma}{dx}\right) - \frac{d}{dy}\,.\left(\frac{1}{q^2}\frac{d\gamma}{dy}\right).$$

Now by substitution we can show that

$$\gamma = \mathrm{A}q^{1/2}\cos\left(pt - \frac{p_0}{c^2}\int(u\,dx + v\,dy)\right). \quad . \quad . \quad (4)$$

is a close approximation to the solution of this equation provided

$$\frac{\lambda}{d}\left(\frac{q_{\text{max.}} - q_{\text{min.}}}{q_{\text{max.}} + q_{\text{min.}}}\right)$$

is a small quantity. λ is the wave-length of the electronic waves, d the distance an electron would travel between the maximum and minimum values of q; u and v are the components of the velocity at x, y of a point charge with the same energy as the electron and exposed to the same field. The reasoning is the same as that given on page 1080. It must be pointed out that u, v are not the components of the velocity of the electron itself at the time t, but the components of the velocity the electron will have when (it may be after a considerable time) it arrives at the point x, y.

From equations (3) and (4) we see that approximately

$$\frac{\mathrm{X}p_0}{c^2}=\frac{\mathrm{A}}{q^{1/2}}\frac{v}{q}\sin\theta,$$

$$\frac{\mathrm{Y}p_0}{c^2}=-\frac{\mathrm{A}}{q^{1/2}}\frac{u}{q}\sin\theta,$$

when

$$\theta=pt-\frac{p_0}{c^2}\int(u\,dx+v\,dy).$$

Hence

$$\mathrm{X}u+\mathrm{Y}v=0,$$

so that the electric force is at right angles to the vector u, v, i. e., it is at right angles to the path which a point charge would travel under the influence of the electric field. The direction of propagation of the waves is at right angles to the electric force and also to the magnetic force; hence it will be along the tangent to the path of the charge. The electronic waves will describe curved paths, and these paths will be the paths of a point electron under the electric field. If ds is an element of this path, then

$$u\,dx+v\,dy=q\,ds$$

and

$$\gamma=\mathrm{A}q^{1/2}\cos\left(pt-\frac{p_0}{c^2}\int q\,ds\right).$$

The phase velocity of these waves is c^2/q, and the group velocity q. Thus on this view a series of waves travelling along the path of the electron, but extending in front of the electron, is an integral part of the electron. The group velocity of these waves at any point is equal in magnitude and direction to the velocity which the electron will have when it reaches that point. We may regard the electron with its charge as a kind of hump on the distribution of electric force in the electronic waves, and that this hump is carried on by these waves with the group velocity of the waves.

When the electron does not describe a closed or re-entrant path, these waves will impose no restriction on the path, and any such path which could be described by a point electron under the influence of the electric field is a possible path of the electron accompanied by its waves. The case is different, however, when the path is re-entrant or closed ; the waves also describe this path, and the electric and magnetic forces in the electronic waves most recur after the circumference has been described.

Thus, as the equation for γ is of the form

$$\gamma = \mathrm{Q} \cos\left(pt - \frac{p_0}{c^2}\int q\,ds\right),$$

where Q is a function of q and the space coordinates, the right-hand side must be the same at the end and the beginning of the circuit. Q will be so automatically, but

$$\cos\left(pt - \frac{p_0}{c^2}\int q\,ds\right)$$

will only be so if

$$\frac{p_0}{c^2}\int_0^{\mathrm{S}} q\,ds = 2n\pi, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where n is an integer and S the circumference of the circuit. The only possible closed paths are those which satisfy this condition.

Let us apply this to the case when the path of the point electron under the action of a force at the focus equal to e^2/r^2 is the ellipse

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1.$$

If $$x = a\cos\phi, \qquad y = b\sin\phi,$$

$$q\,ds = e\sqrt{\frac{a}{m}}(1 - \epsilon\cos\phi)\,d\phi,$$

where

$$\epsilon^2 = \frac{a^2 - b^2}{a^2},$$

and m is the mass of an electron

$$\int_0^{\mathrm{S}} q\,ds = e\sqrt{\frac{a}{m}}\int_0^{2\pi}(1 - \epsilon\cos\phi)\,d\phi = 2\pi e\sqrt{\frac{a}{m}}.$$

Hence, by (5),

$$\frac{p_0}{c^2} 2\pi e \sqrt{\frac{a}{m}} = 2n \cdot \pi$$

or

$$a = \frac{n^2 \cdot m \cdot c^4}{p_0 c^2}.$$

the same type of expression as that given by the ordinary quantum theory.

When the electron is describing an ellipse under a force directly proportional to the distance if the equation to the ellipse is

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1,$$

and

$$x = a \cos \phi, \quad y = b \sin \phi,$$

then

$$q\, ds = \frac{2\pi}{\mathrm{T}} (a^2 \sin^2 \phi + b^2 \cos^2 \phi)\, d\phi,$$

where T is the time the point electron takes to describe an orbit

$$\frac{p_0}{c^2} \int_0^s q\, ds = \frac{2\pi p_0}{\mathrm{T}c^2} \int_0^{2\pi} (a^2 \sin^2 \phi + b^2 \cos^2 \phi)\, d\phi = \frac{2\pi^2 p_0}{\mathrm{T}c^2} (a^2 + b^2).$$

This must equal $2n\pi$ where n is an integer; hence

$$\frac{\pi p_0}{c^2 \mathrm{T}} (a^2 + b^2) = n.$$

When the orbits of the point charges are nearly circular and q therefore approximately constant, the solution takes a simple form. Use polar coordinates r and θ; if R and T are respectively the radial and tangential components of the electric force in the wave, the wave equations (3) become

$$\mathrm{R} \frac{p_0^2}{c^4} q^2 = ip \frac{d\gamma}{r\, d\theta},$$

$$\mathrm{T} \frac{p_0^2}{c^4} q^2 = -ip \frac{d\gamma}{dr},$$

$$\frac{d\mathrm{T}}{dr} - \frac{d\mathrm{R}}{r\, d\theta} = ip\gamma.$$

A solution of these is

$$\gamma = A \cos(pt - k\theta),$$

$$R = \frac{Akpc^4}{rp_0^2q^2}\cos(pt - k\theta),$$

$$T = 0,$$

$$k = \frac{p_0}{c^2}qa,$$

when a is the mean value of r.

Since γ must be unaltered when θ increases by 2π,

$$k2\pi = 2n\pi,$$

where n is an integer.

Thus

$$\frac{p_0qa}{c^2} = n,$$

which is equivalent to the usual quantum relation.

When the orbit of the point electron is a closed curve, the electronic waves of electric and magnetic force flow in closed curves; the energy in these waves travels tangentially round and round these curves, so that there is no radiation and no loss of energy. Thus, the moving electron will only radiate when it escapes from the closed circuit.

By equation (3) we have

$$\left(\frac{dX}{dx} + \frac{dY}{dy}\right)q^2 + \left(X\frac{dq^2}{dx} + Y\frac{dq^2}{dy}\right) = 0.$$

If ρ is the density of the electrification, X_0, Y_0 the components of the applied force,

$$\frac{dX}{dx} + \frac{dY}{dy} = 4\pi\rho; \quad \frac{dq^2}{dx} = \frac{2X_0e}{m}, \quad \frac{dq^2}{dy} = \frac{2Y_0e}{m}.$$

Thus

$$4\pi\rho q^2 + \frac{2e}{m}(XX_0 + YY_0) = 0,$$

now

$$XX_0 + YY_0 = EF\cos\psi,$$

where E is the resultant electric force in the electronic waves F the resultant applied external force, and ψ the angle between E and F. E is at right angles to the path of the point electron under the external force; hence $F\cos\psi$ is the component of the external force along the normal to the path, so that if S is the radius of curvature of the path,

$$\frac{mq^2}{\mathrm{S}} = \mathrm{F}e\cos\psi\,;$$

so that

$$2\pi\rho\mathrm{S} + \mathrm{E} = 0.$$

E is proportional to

$$q^{-\frac{1}{2}}\cos\left(pt - \frac{p_0}{c^2}\int q\,ds\right);$$

hence ρ varies as

$$\frac{1}{\mathrm{S}\sqrt{q}}\cos\left(pt - \frac{p_0}{c^2}\int q\,ds\right).$$

The Passage of Electronic Waves through Crystals.

We regard the crystal as a system of atoms arranged in a series of parallel planes at a distance b apart, the arrangement in any one plane being a replica of that in any other. Take the axis of y at right-angles to these planes. Then the properties of the atom are periodic, and can be represented by expressions of the form

$$\alpha_1\cos\frac{2\pi}{b}y + \alpha_2\cos\frac{4\pi}{b}y + \;\ldots\ldots$$

We shall confine ourselves at first to the case where there is only one harmonic term.

The effect of these atoms on the density of the electronic atmosphere will be to make the quantity which is equal to p_0^2 for the electron in free space become —

$$p_0^2\left(1 - \alpha\cos\frac{2\pi}{b}y\right)$$

for the electronic waves inside the crystal. The quantity α will be measured by the work required to drag an electron out of a crystal divided by $mc^2/2$.

Consider now an electron moving in the plane of xy. Let the electronic electric waves be plane polarized and suppose the electric force is in the plane of xy. The magnetic force γ will be at right angles to this plane, and will, if the wave-length is so small that the energy of the electron only changes by a small fraction in a wave-length, satisfy the equation

$$\frac{d^2\gamma}{dx^2}+\frac{d^2\gamma}{dy^2}+\frac{1}{c^2}\left(p^2-p_0^2+p_0^2\alpha\cos\frac{2\pi}{b}y\right)\gamma=0. \quad . \quad (1)$$

γ is supposed to vary as ϵ^{ipt}.

Let the electronic waves outside the crystal, *i.e.*, where $\alpha=0$, be represented by

$$\gamma=\cos\left(pt-\frac{2\pi}{\lambda}(x\cos i+y\sin i)\right),$$

where i is the angle the incident beam makes with the axis of x.

Substituting this value, we find

$$\frac{4\pi^2}{\lambda^2}=\frac{1}{c^2}(p^2-p_0^2).$$

Put, in equation (1),

$$\gamma=w\epsilon^{\frac{-i2\pi x\cos i}{\lambda}},$$

where w is a function of y only ; then (1) becomes

$$\frac{d^2w}{dy^2}+\left(\frac{4\pi^2}{\lambda^2}\sin^2 i+\alpha'\cos\frac{2\pi y}{b}\right)w=0, \quad . \quad . \quad . \quad (2)$$

where

$$\alpha'=\frac{p_0^2}{c^2}\alpha.$$

Putting $\eta=\frac{\pi y}{b}$, (2) becomes

$$\frac{d^2w}{d\eta^2}+(\Theta_0+2\Theta_1\cos 2\eta)w=0, \quad . \quad . \quad . \quad (3)$$

where

$$\Theta_0=\frac{4b^2}{\lambda^2}\sin^2 i, \quad 2\Theta_1=\frac{b^2}{\pi^2}\alpha'=\frac{b^2p_0^2}{c^2\pi^2}\alpha.$$

This is a special case of Hill's equation. Hill's solution is ('Acta Mathematica,' viii. p. 1, 1886)

$$w=\Sigma A_n\epsilon^{ic\eta}\epsilon^{i.2n\eta}\,*,$$

where n is an integer. Thus the only waves possible form a discrete set, such that the wave-length λ is expressed by

$$\frac{2\pi}{\lambda}=(c+2n)\frac{b}{\pi},$$

where n is an integer.

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* In what follows c is Hill's constant and not the velocity of light.

The quantity c is given by the equation

$$\frac{1-\cos\pi c}{1-\cos\pi\sqrt{\Theta_0}}=\square\,(0), \quad . \quad . \quad . \quad . \quad (4)$$

where $\square$ is a determinant with an infinite number of rows. Retaining squares, but neglecting higher powers of Θ_1, Hill proves that

$$\square\,(0)=1+\pi\frac{\cot\frac{1}{2}\pi\sqrt{\Theta_0}}{4\sqrt{\Theta_0}}\times\frac{\Theta_1^2}{1-\Theta_0}, \quad . \quad . \quad . \quad (5)$$

$$c^2=1+\sqrt{(\Theta_0-1)^2-\Theta_1^2}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus, if we neglect the squares of Θ_1, $\square\,(0)=1$, and from (4)

$$c=\sqrt{\Theta_0}=\frac{2b\sin i}{\lambda},$$

$$c\eta=\frac{2\pi\sin i\,.\,y}{\lambda}.$$

The term $\epsilon^{ic\eta}=\epsilon^{\frac{i(2\pi\sin i\,.\,y)}{\lambda}}$, and thus represents the original wave propagated without change of wave-length. Hence, if we neglect Θ_1^2, there is no change produced by the crystal in the refractive index. Where Θ_1 is large enough to make c differ from $\sqrt{\Theta_0}$, $c\eta$ will no longer be equal to $2\pi\sin i\,.\,y/\lambda$ and the wave-length of the electronic wave in the crystal will differ from that outside. Thus there will be an appreciable refractive index.

Taking the primary wave in the crystal as represented by $\cos c\eta$, and writing equation (8) in the form

$$\frac{d^2w}{d\eta^2}+\Theta_0 w+2\Theta_1\cos 2\eta w=0,$$

and putting $w=\cos c\eta$ in the last term, we have

$$\frac{d^2w}{d\eta^2}+\Theta_0 w+\Theta_1\cos(c+2)\eta+\Theta_1\cos(c-2)\eta=0\,;$$

hence

$$w=\frac{\Theta_1\cos(c+2)\eta}{(c+2)^2-\Theta_0}+\frac{\Theta_1\cos(c-2)\eta}{(c-2)^2-\Theta_0}+\cos c\eta.$$

Restoring the factors involving x and t, and putting for η its value $\pi y/b$,

$$w = \frac{\Theta_1 \cos\left\{pt - 2\pi\left(\frac{x\cos i}{\lambda} + \frac{(c+2)y}{2b}\right)\right\}}{(c+2)^2-\Theta_0}$$

$$+ \frac{\Theta_1 \cos\left\{pt - 2\pi\,.\left(\frac{x\cos i}{\lambda} + \frac{(c-2)y}{2b}\right)\right\}}{(c-2)^2-\Theta_0}$$

$$+ \cos\left\{pt - 2\pi\left(\frac{x\cos i}{\lambda} + \frac{c\,.\,y}{2b}\right)\right\}, \quad . \quad . \quad (7)$$

the third term representing the primary wave; hence the primary wave is accompanied by two waves, the direction of propagation of the primary one being between the directions of the secondary ones, and its wave-length being also intermediate between those of its secondaries. One or other of these secondaries becomes important when either $(c+2)^2-\Theta_0$ or $(c-2)^2-\Theta_0$ vanish. Θ_0, as we have seen, is equal to $2b\sin i/\lambda$.

We shall leave the general case for the present and consider the very important special case where Θ_1 is so small that its square may be neglected. In this case, as we have seen,

$$c^2 = \Theta_0 = \frac{4b^2\sin^2 i}{\lambda^2}.$$

The primary wave is now

$$\cos\left\{pt - \frac{2\pi}{\lambda}(x\cos i + y\sin i)\right\}.$$

The secondary waves are

$$\left.\begin{array}{c} \dfrac{\Theta_1\cos\left\{pt - \dfrac{2\pi}{\lambda}\left(x\cos i + y\sin i + \dfrac{\lambda}{b}\right)\right\}}{4c(c+1)} \\[3ex] \dfrac{\Theta_1\cos\left\{pt - \dfrac{2\pi}{\lambda}\left(x\cos i + y\sin i - \dfrac{\lambda}{b}\right)\right\}}{4c(c-1)} \end{array}\right\} . \quad . \quad (8)$$

The second of these increases rapidly as c approaches 1.

We can find the value of $\Theta_1/(c-1)$, $c \to 1$ as follows. By (5),

$$\Box(0) = 1 + \pi\frac{\cot\frac{1}{2}\pi\sqrt{\Theta_0}}{4\sqrt{\Theta_0}} \times \frac{\Theta_1^{\,2}}{1-\Theta_0}.$$

Let $\Theta_0=1+\epsilon$, where ϵ is small; then

$$\frac{\cot\frac{1}{2}\pi\sqrt{\Theta_0}}{4\sqrt{\Theta_0}}=-\frac{\pi}{16}\epsilon,$$

so that
$$\square(0)=1+\frac{\pi^2}{16}\Theta_1^2,$$

and
$$\frac{1-\cos\pi c}{1-\cos\pi\sqrt{\Theta_0}}=1+\frac{\pi^2}{16}\Theta_1^2.$$

Let $c=1+\theta$, where θ is small; then, when $\Theta_0=1$,

$$-\frac{\pi^2\theta^2}{4}=\frac{\pi^2}{16}\Theta_1^2 \qquad \text{or} \qquad \theta=\sqrt{-1},\ \frac{\Theta_1}{2},$$

$$c=1+\sqrt{-1}\frac{\Theta_1}{2}.$$

Substituting this value of c in (8), and noticing that, since $\Theta_0=1$, $\lambda/b=2\sin i$, the expression for one of the secondary waves is

$$\tfrac{1}{2}\epsilon^{-\Theta_1\frac{\pi y}{2b}}\sin\left(pt-\frac{2\pi}{\lambda}(x\cos i-y\sin i)\right).$$

This represents a wave travelling in the direction in which the primary wave would travel if reflected by a mirror parallel to $y=0$. There is a change in phase of $\pi/2$. The intensity diminishes slowly as y increases. The maximum value of the amplitude is half that of the primary wave. The expression given in (8) for the primary wave is on the assumption $c=1$. If the next approximation is taken there will be the factor $\epsilon^{-\Theta_1\frac{\pi y}{2b}}$ in the expression for the amplitude of the primary wave. The condition that the secondary wave should be comparable with the primary, viz., $\lambda=2b\sin i$, is the well-known one for diffraction of waves by a crystal.

The preceding investigation is based on the assumption that Θ_1 is small. This, as we have seen, requires the refractive index of the medium to be unity; for large values of Θ_1. c^2 would no longer be equal to Θ_0 and there would be an appreciable refractive index. The primary wave is represented by the term $\epsilon^{ic\eta}$. Now

$$c\eta=\frac{c\pi y}{b}=\frac{c}{\sqrt{\Theta_0}}\,\frac{2\pi y\sin i}{\lambda},$$

so that the primary wave restoring the factors depending on x and t will be

$$\cos\left(pt-\frac{2\pi}{\lambda}\left(x\cos i+\frac{c}{\sqrt{\Theta_0}}\sin i\right)\right).$$

This may be written as

$$\cos\left(pt-\frac{2\pi}{\lambda'}(x\cos i'-y\sin i')\right),$$

if

$$\frac{\cos i}{\lambda}=\frac{\cos i'}{\lambda'},$$

$$\frac{c}{\sqrt{\Theta_0}}\,\frac{\sin i}{\lambda}=\frac{\sin i'}{\lambda'},$$

or

$$\frac{1}{\lambda_1}=\frac{1}{\lambda}\sqrt{\cos^2 i+\frac{c^2}{\Theta_0}\sin^2 i}.$$

If μ is the refractive index of the medium, $\mu=\lambda/\lambda'$, hence

$$\mu^2=\cos^2 i+\frac{c^2}{\Theta_0}\sin^2 i.$$

$$\cos^2 i+\frac{\lambda^2}{4b^2}\left(1+\sqrt{(\Theta_0-1)^2-\Theta_1^{\,2}}\right)$$

by equation (6).

Thus μ depends upon the angle of incidence and the wave-length.

When $\Theta_0-1<\Theta_1$ there is an imaginary part in the expression for μ^2. When Θ_0-1 is large compared with Θ_1,

$$\mu^2=1-\frac{\lambda^2}{8b^2}\,\frac{\Theta_1^{\,2}}{\Theta_0-1}.$$

We see from equation (7) that for the diffracted wave

$$(c-2)^2=\Theta_0,$$

$$c-2=-\sqrt{\Theta_0};$$

from this and equation (6), $\sqrt{\Theta_0}$, *i.e.*, $2b\sin i/\lambda$ can be found.

The value of Θ_1 can be expressed in terms of the work required to remove an electron from the crystal. If this work is expressed as V-electron volts, then in (1) $\alpha=2\mathrm{V}e/mc^2$. Hence,

$$2\Theta_1=\frac{2\mathrm{V}e\times10^8\times b^2p_0^{\,2}}{c^2\pi^2\,.\,mc^2},$$

$$p_0=2\pi\,.\,1{\cdot}2\times10^{20}\quad\text{if}\quad b=10^{-8}.$$

This makes

$$2\Theta_1=\frac{\mathrm{V}}{40}\quad\text{or}\quad\Theta_1=\frac{\mathrm{V}}{80}.$$

CXI. *Heats of Dissociation and Absorption Spectra of some Complex Molecules.*

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ONE of the outstanding problems in photochemistry is the relationship between the thermal energy required to decompose a substance and the minimum of light energy necessary to bring about the same transformation. The one is usually calculated in terms of energy of binding or heat of linking from thermochemical data, or from energy of activation, and the other from certain limits in the absorption spectrum, or from the commencement of certain regions of photoactivity in the spectrum. Such comparisons have invariably been misleading. One was accustomed to think of thermal decomposition in terms of nuclear separations following on considerable changes in the rotational and vibrational energy in the molecule. The photochemical decomposition was related to orbital changes in one or more of the valency electrons, and although such a process must also involve nuclear separations, the relationship between the two was not always clearly perceived. Only the simpler photochemical changes coming within the boundary of Einstein's law of the Photochemical Equivalence could lend themselves to such a study. The majority of photochemical reactions are very complicated, and involve transfers of energy so rapid as to obscure the original, primary process.

Within recent years a great deal seems to have been cleared up with regard to heats of dissociation and photochemical energy in the case of the simpler molecules. From a study of the absorption spectra of the halogen molecules Franck (Trans. Farad. Soc. xxi. p. 536, 1926) was able to conclude that the primary dissociation into atoms began at a certain region of the spectrum. This region was the convergence limit of the series of oscillation bands characteristic of the molecule. Beyond this limit there was a zone of continuous absorption where complete dissociation into atoms occurred (Mecke, *Ann. d. Phys.* lxxi. p. 104, 1924; Dymond, *Z. Physik*, xxxiv, p. 553, 1925;

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* Communicated by Prof. F. G. Donnan, F.R.S.

Kuhn, *Z. Physik*, xxxix, p. 77, 1926). The atoms were not necessarily normal atoms, that is, atoms in the lowest quantum state. In order to account for the fact that at the convergence limit the quantum of light-energy was greater than the heat of dissociation, Franck postulated that one of the atoms was in an excited or metastable state. The energy of excitation was calculated from the difference of the two terms 2^2P_2 and 2^2P_1, and satisfactory agreement was found between the experimental and calculated values (Turner, Phys. Rev. xxvii, p. 397, 1926).

The dissociation, of course, involves a separation of the two nuclei of the atoms, and this possibility depends on the magnitude of the oscillational and rotational energy changes which are coupled with the changes in energy of the electron system due to the absorption of light. If the electron jump is very rapid compared with the slow vibration of the nuclei, and a greatly changed strength of binding occurs, the nuclei may acquire such large amounts of potential energy that the new state of vibration set up may actually bring about their separation (Condon, Phys. Rev. xxvii, p. 640, 1926). All molecules, however, do not dissociate as readily as this even after receiving amounts of energy far exceeding the energy of dissociation. They may exist for some time in excited states far removed from the normal and energy may be re-admitted in the form of molecular fluorescence (*e. g.*, I_2, H_2, etc.). Sometimes a collision during the life of an excited molecule may bring about its dissociation. This is the mechanism postulated by Stern and Volmer (*Zeit. für wissen. Photog.* xix. p. 275, 1920).

The majority of bonds or linkages in molecules which interest the photochemist usually belong to either of the two classes, polar or non-polar. It is possible to learn a great deal about the mode of dissociation of molecules having one or other of these linkages from a study of their absorption spectra. Wherever we find a zone of continuous absorption we are led to expect an elementary dissociation process not involving the collision mechanism of Stern and Volmer, and the long-wave length limit of this absorption band will be related to the heat of dissociation of the molecule in two ways, according to the nature of the linkage, polar or non-polar. For a polar bond, as shown by Franck, Kuhn, and Rollefson (*Zeit. Physik*, xliii.

p. 155, 1927), the heat of dissociation *may* be equal to the energy calculated from the long-wave length limit. This is the case for the alkali halides, and dissociation into two normal atoms is to be expected in the first range of the spectrum. For a non-polar bond, *e. g.*, Ag=I, H=I (Franck and Kuhn, *ibid.* p. 164), the long-wave limit corresponds to the heat of dissociation plus an amount of energy necessary to excite one of the atoms.

These observations have been confined to diatomic molecules. With more complicated molecules very great difficulties might be experienced with the treatment of the subject owing to the increase in the number of linkages and the more complex nature of the oscillational and rotational energy changes. In a special case, however, where a zone of continuous absorption was due to electronic activation at some particular linkage in a molecule, it was considered that the dissociation process might be analogous to the disruption of a diatomic molecule. Organic compounds containing carbon and hydrogen and one non-polar carbon-iodine bond might furnish molecules of this kind. The absorption spectra of their vapours are known to be continuous (Pauer, *Ann. der Phys.* lx. p, 363, 1897 ; Purvis, Jour. Chem. Soc. xcix. p. 2319, 1911), and they appear to dissociate with the liberation of iodine in the long-wave region (Job and Emschwiller, *Compt. Rend.* clxxix. p. 52, 1924 ; Iredale, Jour. Phys. Chem. xxxiii. p. 290, 1929). Moreover, within the limits of experimental error, the photochemical decomposition, as in the case of hydrogen iodide, agrees with the law of the photochemical equivalence.

Now the absorption spectrum of hydrogen iodide has been shown to be continuous (Bonhoeffer and Steiner, *Zeit. Phys. Chem.* cxxii. p. 287, 1926 ; Tingey and Gerke, Jour. Amer. Chem. Soc. xlviii. p. 1838, 1926), and the long-wave length limit fairly definitely established. In continuation of the earlier work of Warburg (*Sitz. Akad. Wiss. Berlin*, ccc. p. 1918) Lewis (Jour. Phys. Chem. xxxii, p. 270, 1928) has shown that the photochemical dissociation of HI in the initial stage is independent of collisions, and Bodenstein and Linweig (*Zeit. Physik. Chem.* cxix. p. 123, 1926) have shown that the mechanism is independent of the state of aggregation of the molecules ; within the limits of experimental error it seems that the mode of dissociation is the same in the liquid as in the gaseous state, and the long-wave limit of the absorption appears to be the same. This, however, would not be quite correct. The heat of dissociation in the liquid state differs from that in the gaseous state according to conventional thermochemical calculations by an amount which is of the order of the molecular heat of vaporization of the liquid.

When we come to examine organic compounds containing the C-I bond experimental difficulties are realized owing to the excessively long columns of the vapours which must be used before an absorption limit can be detected. This is practically also the case with HBr and HI (Tingey and Gerke, *loc. cit.*), though a fairly satisfactory limit seems to have been established in the case of HI. Now the thermochemical data for organic iodine compounds which serve as a basis for the calculation of energy of binding or heat of dissociation of the C–I bond are only available to any degree of accuracy for the substances in the liquid state. We have therefore measured the absorption limits in the liquid state also, which may be open to some objections. As, however, we are not studying band spectra, the continuous absorption in the liquid may be considered to be similar to the continuous absorption in the vapour. The difference in the absorption limits, if any, will be related to the difference in the total energy of the molecule in the two states as affects the oscillation energy of the two nuclei at the place of disruption of the molecule. All that can be said is that this difference is of the order of the molecular heat of vaporization. The molecules in the liquid state appear to be simple ; there is no polymerization involving the valency electron (Turner, Molecular Association, lxx. p. 101, 1915).

EXPERIMENTAL.

The absorption measurements were carried out with a Hilger medium quartz spectrograph. As sources of light both the quartz mercury vapour lamp and the condensed carbon spark have been employed. A biprism in front of the slit was used in conjunction with a sector photometer. In the measurements of the absorption limits no rotation of the sectors was, of course, actually employed, and these limits were ascertained with a fair degree of accuracy by comparing the densities of the photographs of the two spectra in the region where the absorption commenced. Layers of the liquids 1 cm. and 4 cm. in length were used in conjunction with an empty comparison tube, and it was assumed that the loss of intensity through reflexion and absorption by the quartz cover plates, etc., would be the same in the two cases. A slight, and in the present case insignificant, error would arise through having a change of medium quartz-air in the one cell and quartz-liquid in the other. The loss of light by scattering was difficult to ascertain, but it was compensated for in the visible, non-absorbable region of the spectrum by adjusting the photometer to give equal photographic densities of the two comparison spectra in the negative. The negatives were examined with the aid of a strong light through a plate of opalized glass, and also with a Moll recording microphotometer.

Great care was taken to purify the iodides, and after the last traces of iodine were removed many careful distillations under diminished pressure were resorted to in order to

TABLE I.

Heats of combustion (in kilogram calories per gram-molecule) (K).

Methane	(gas)	211	Methyl iodide	(liquid)	195
Ethane	,,	368	Ethyl iodide	,,	356
Propane	,,	526	Iso-propyl iodide	,,	509
Propylene	,,	490	Allyl iodide	,,	478
Benzene	,,	787	Iodobenzene	,,	771

Heat of combustion of carbon	94·38
,, ,, ,, hydrogen (H)	34·19
,, sublimation ,, carbon	150*
,, ,, ,, iodine (I)	7·5
,, dissociation ,, hydrogen (H)	50·5
,, ,, ,, iodine (I)	17·6

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* The value for the heat of sublimation of carbon is given in the International Critical Tables as 152 K. Kohn and Guckel (*Zeit. Physik*, xxvii. p. 305, 1924) arrive at a value 139 K. ± 7 per cent. (see also Herbst, *Zeit. Physik*, xxvii. p. 366, 1926). Older values varied from 120 to 200 K. or more. From a consideration of all the available data we take 150 K. as a more probable value.

obtain pure products. Iodine is easily liberated by heat under certain conditions, and slow decomposition often takes place at ordinary temperatures. The addition of silver foil prevents the formation of colour due to liberated iodine.

The heat of linking or binding of carbon and iodine was calculated from the published data on the heats of combustion of organic iodine compounds. (Berthelot, *Ann. Chim. Phys.* (7) xxi. p. 296, 1900; International Critical Tables, vol. v. 1929). In common with other thermochemical data these are not very satisfactory. Other investigators have not always given the fundamental standards on which their calculations of the heats of binding depend, and as these have altered to some extent during the past few years, we include here to avoid ambiguity a list of the data we have used as a foundation for our calculations.

In the table which follows λ in $\mu\mu$ is the long wave-length limit of the absorption band, Q is the heat of binding in kilo-calories calculated from thermochemical data, and D the heat of dissociation calculated from the absorption limit, taking into account the energy (22 K.) necessary to excite the iodine atom.

TABLE II.

	λ.	Q.	D.
Methyl iodide	395	50	50
Ethyl iodide	413	46	47
Iso-amyl iodide	413	—	47
Iso-propyl iodide	—	50	—
Iodobenzene	415	49	46
(Allyl iodide)	($>$440)	45	($<$42)
(o-Iodotoluene)	($>$420)	—	($<$46)

The values for allyl iodide and iodotoluene are enclosed in brackets. We were not certain of the purity of these particular liquids, and a minute trace of coloured impurity may modify their optical properties considerably.

It is impossible to believe that the heat of solution of the products of photodecomposition can enter as a term into the equation for the heat of dissociation, as the redistribution of energy in this case would be established through the agency of molecular collisions which do not affect the primary process. See, however, Franck and Scheibe (*Zeit. Phys. Chem.* cxxxix. p. 22, 1928), who discuss the formation of an atom of iodine from an ion in an aqeuous medium. It is remarkable that these authors do not consider the possibility of chemical action between the iodine atom and a water molecule, which may have a large heat of reaction. This may be the beginning of a series of chain reactions, and it is surely impossible to learn anything of these from a study of the absorption spectrum.

The values of Q show no intelligible variation among themselves. D varies in a way that might be expected if we consider the binding of C and I to be influenced by the binding of adjacent carbon atoms.

We have said that the absorption is continuous for the vapours of these iodides. This matter certainly needs further investigation, and we hope to continue these studies when suitable equipment is available. It is possible that with molecules having large moments of inertia absorption spectra may sometimes have the semblance of continuity. This will depend on the resolving power of the spectrograph.

Taking the data of Pauer (*loc. cit.*) and Purvis (*loc. cit.*) for iodobenzene, and plotting the absorption limits against the pressure of the vapour, it is easily seen that the limit converges to some wave-length beyond 400 $\mu\mu$.

In all these cases the selection of an absolute wave-length limit would be a somewhat arbitrary proceeding. There must be some molecules possessing internal energy greater than the average. A complete theory of the subject should take into account not only the shift, if any, of the absorption band, but also, perhaps, the variation in the heat of dissociation with the temperature.

We have to thank Miss E. Stobo, B.Sc., for some assistance in purifying the iodides, and the Trustees of the Commonwealth Science and Industry Endowment Fund for a grant of money for the purchase of certain apparatus.

The University of Sydney.

CXII. *A New Inertia-less Chronograph.* *By* P. A. Cooper, *Research Department, Woolwich*[*].

[Plate XVIII.]

Much interest has been shown during the last few years in gas-discharge lamps of the G.E.C. "Osglim" type. Their electrical characteristics have been examined in detail, notably by S. O. Pearson and H. St. G. Anson[†], M. A. Oschwald and A. G. Tarrant[‡], J. H. Shaxby and J. C. Evans[§], and J. Taylor and W. Clarkson[||].

Pearson and Anson first described how they could be used for the production of relaxation oscillations. Attempts to apply the principle, however, have never been entirely successful because of the uncertain delay which occurs between the instant at which the requisite voltage is applied to the lamp and that at which the discharge strikes. Since the glow surrounding the cathode is the visible counterpart of this discharge, it was to be expected that attempts to use them for photographic recording might be open to the same objection. Fortunately though it is just as easy to record an event by extinguishing a lamp as by energizing it, and in the early experiments that was always the method used. It was done by connecting the lamp across approximately one-half of a non-reactive resistance bridging a 500-volt D.C. circuit. The event was recorded by short-circuiting the lamp and that part of the resistance in parallel with it, the other part acting solely as a current-limiting device. This method worked quite satisfactorily, but has long been superseded by others of more general utility.

The delay to which reference has been made had claimed a considerable amount of attention and various ways in which it might be minimized had been proposed[¶]. However, none of these suggested methods involving the use of ultra-violet light, X-rays, or of radioactive compounds were really successful, because the initial ionization which it was their function to produce was not sufficiently intense. A far more satisfactory way of dealing with this difficulty, and one by which the lag in lighting up can be reduced to a negligible amount, is by the use of what might be called a pilot circuit, since it plays very much the same part as the pilot jet in an incandescent gas lamp. This principle has been incorporated in all the circuits to be described and it has made it possible to record events by lighting up lamps just as accurately as by putting them out.

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[*] Communicated by the Author.

[†] Proc. Phys. Soc. xxxiv.

[‡] *Ibid.* xxxvi.

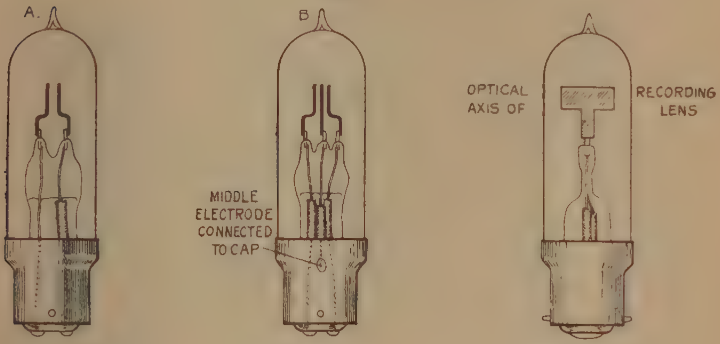
[§] *Ibid.*

[||] *Ibid.*

[¶] *Loc. cit.*

The Osglim lamp is not well adapted for photographic recording; in all probability it was never developed for any other purposes than lighting and advertising. The discharge takes place in a mixture of helium and neon giving a light which, for photographic work, would necessitate the use of panchromatic emulsion and this, for routine purposes, has its disadvantages. Because of this it was decided to use lamps having an argon filling, since this gives the blue light to which ordinary emulsion is most sensitive. The first type of lamp specially made by the G.E.C., Ltd., Wembley, to a sketch supplied by this Department, is shown in fig. 1, A. The electrodes, following standard G.E.C. practice, were clean iron plates. They were placed about 1/10 inch apart and were as long as could conveniently be used. This point is important because it is

Fig. 1.



Front view of single cathode lamp.

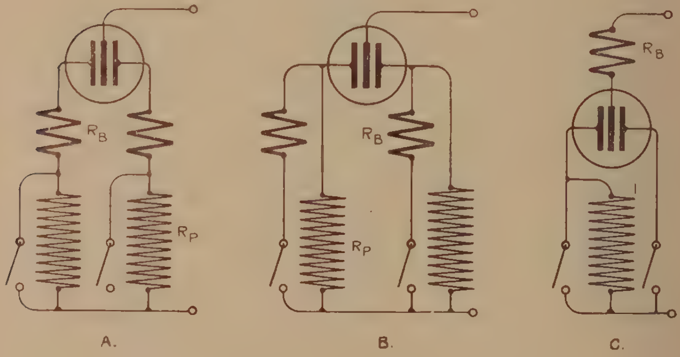
Front view of double cathode lamp.

Side view of either lamp.

by looking along the cathode edgeways that one gets the highest intrinsic brightness. Early in 1927 this type was replaced by that shown in fig. 1, B. It comprises a single anode mounted between two separate cathodes, each of which can be made to glow quite independently of the other. The cathodes are connected to the lead contacts in the cap of the lamp, and the anode to the brass cap itself. This arrangement is virtually two lamps in the same glass envelope.

Fig. 2 shows three modifications of the basic circuit which has been developed for time-recording with make and break contacts or with a combination of both. As with all discharge tubes, arc lamps and the like operating from a continuous supply, ballast resistances are necessary to limit the magnitude of the discharge currents. These usually take the form of 110-volt 16-c.p. carbon lamps having a reasonably non-inductive resistance of about 400 ohms; they are designated R_B. The pilot circuit principle can easily be traced in each of the three modifications shown. The pilot leak R_P, usually of 50,000 ohms resistance passes sufficient current to keep the argon filling ionized but not enough to give a photographic record with the film speeds used. The circuit shown in fig. 2, C is unsymmetrical in the sense that only one such pilot leak is used, in association with one of the two

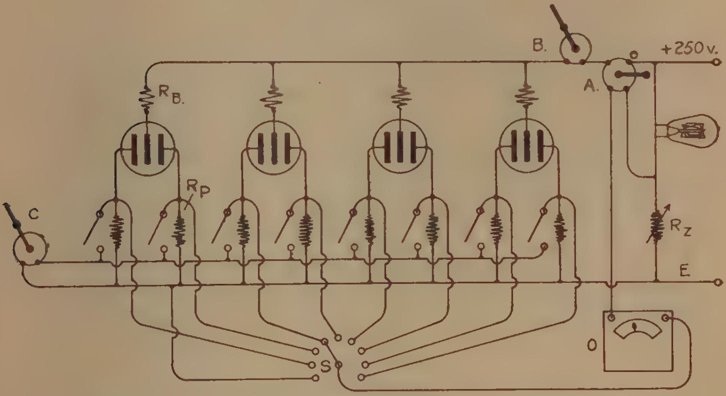
Fig. 2.



cathodes; as long as the requisite ionization is present within the lamp it does not matter much where it is located.

Fig. 3 shows a bank of double cathode lamps incorporated in a circuit suitable for routine work. For the sake of clearness the leads to the contacts have been kept very short, though actually, as used in a particular piece of experimental work to which this apparatus has been applied, they are air-lines approximately three-quarters of a mile long. O is a milliammeter, calibrated as an ohmmeter, the resistance R_Z being variable in order that the instrument may be used on mains having different voltages (220–250 D.C.).

Fig. 3.



Although the discharge lamps are not excessively overrun it is desirable to conserve them as far as is conveniently possible. This is the function of the switches B and C, the latter being closed just before the records are to be taken, and the former opened immediately afterwards. They are operated by a falling weight, the motion of which is correlated with the opening of the camera shutter; such arrangements have often been used before in work of this nature and do not call for detailed description. Four double lamps only have been shown in the figure, though usually they are assembled in banks of nine behind two slits 1/32-inch wide and $1\frac{3}{4}$ inch apart. The four lamps behind one slit are staggered with respect to the five behind the other in order to keep the records properly spaced. The lens usually fitted is a kinematograph-taking lens of aperture 1/*f* 1·9 and focal length 2 inches, placed about 15 inches in front of the lamps. For routine work the film speed is 5 metres/second, and the uncertainty with which short time intervals are recorded amounts to less than 1/50,000 second. With picked lamps and a little more care the film speed can be doubled and the uncertainty halved. The developer used is the Maximum Contrast Hydroquinone Developer given in the British Journal Photographic Almanac.

Fig. 4 A.

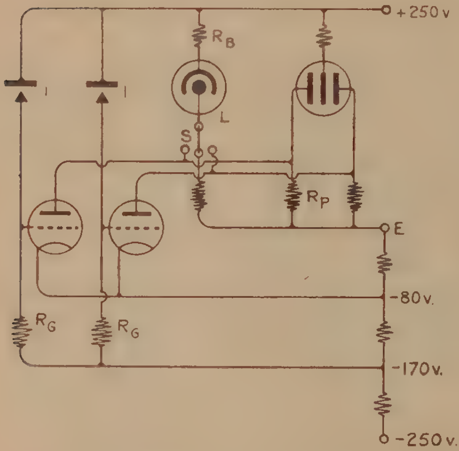
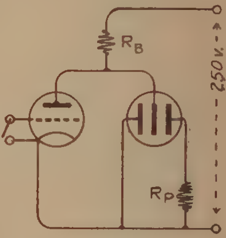


Fig. 4 B.



It is not always convenient to use simple make and break contacts and sometimes, even when this can be done, the resistance of the circuit is too high to allow the lamp to light up properly. In cases of this kind it is convenient to use such an arrangement as that shown in fig. 4, A in which each of the cathodes of a double lamp is connected to the plate of a low-impedance thermionic valve. This circuit has been used very successfully for recording the instants at which ionization currents begin to flow. The ionization gaps I are wired in series with high resistances R_G, the common point between them being connected to the grid of the appropriate valve. Until the instant at which the gas insulation in a particular gap breaks down, the grid of the valve associated with it is strongly negative. When, however, the gap becomes conducting, the potential of the grid becomes more positive and allows current to flow through the valve and that side of the lamp in series with it. A different kind of testing gear has been incorporated in this circuit. It consists of an Osglim lamp L, which can be placed in parallel with either side of the argon lamp used for recording. Since the Osglim lamp strikes at a voltage less than the lower critical voltage of the argon lamp, it takes the whole of the current.

During the actual process of recording, the switch is placed in the neutral position shown in the figure. Pl. XVIII. shows a typical record given by this arrangement. It will readily be appreciated that it can be adapted to many other purposes if the circuit constants are altered to suit the particular conditions.

The one disadvantage attached to the use of the circuit just described lies in the fact that its successful operation necessitates a source of supply of at least 300 volts. Where only one-half of a three-wire D.C. supply system is available it is preferable to use a parallel arrangement of valve and lamp, the essential parts of which are shown in fig. 4 B. The ballast resistance R_B in many cases can with advantage be replaced by an iron-cored choke having the same D.C. resistance and a low value of self capacity.

For all ordinary work the time-trace is provided by a 50 cycles/sec. tuning-fork, and although it is of the vibrating contact type it can be relied upon to give results correct to well within 1 per cent. Where the highest attainable accuracy is required this will be given by a valve maintained elinvar fork circuit now in course of development.

In conclusion, the writer would like to acknowledge his indebtedness to Dr. G. Rotter, C.B.E., and to Dr. R. Ferguson for their never-failing encouragement, without which this work would not have been possible. He is much indebted, too, to the Director-General of Artillery for permission to offer this paper for publication.

CXIII. *A Quartz Suspension Galvanometer for use in D.C. and A.C. Circuits.*

By D. R. Barber, *B.Sc.*, *A.Inst.P.*, 1928–29 *Andrew Simon Research Scholar, University College of the South-West of England, Exeter**.

INSTRUMENTS used in the detection and measurement of very small currents should possess the dual characteristic of high sensitivity combined with inherent stability. The instrument described in the present paper possesses these qualities, and has been developed for measuring either direct or low frequency alternating currents within the range 10^{-3} to 10^{-6} ampere.

The principle utilised is somewhat analogous to that of the quadrant electrometer, since the deflexion is produced by a torsional couple applied to a stretched fibre of quartz, the initial impulse being derived from the motion of two soft-iron armatures symmetrically arranged with respect to the suspension, and floating within two solenoids carrying the current to be detected. The chief advantage of such an arrangement is the high value of torque attainable for weak induction effects—an essential condition if the moving system is to effectively respond at the lower limit of the current range. The suspension fibre is anchored at both ends, and this arrangement is found to give additional mechanical strength to the moving system without unduly lowering the sensitivity of the instrument. The use of quartz in the construction of the rotor assembly ensures a negligible zero error and the elimination of any disturbing temperature effects.

Description of the Instrument.

The instrument is diagrammatically shown in fig. 1 (*a*) representing the plan, and (*b*) the medial section.

A rhomboidal beam of quartz rod, A, 1 mm. diameter, carries at its extremities two soft-iron wires, B, bent into arcs of radius 2·5 cm. and length 1·5 cm. These form the two armatures and are able to move in a horizontal plane within the two solenoids, S_1 and S_2, consisting of a pair of telephone bobbins of which the total resistance is 2000 ohms approximately. A concave mirror, M, is attached to the beam, A, in order that the deflexions of the instrument may be read by the orthodox lamp and scale method. The whole of the rotating framework is rigidly attached to a quartz fibre, C, diameter 10 μ, length 3·2 cm., stretched vertically between the two extremities of a rectangular quartz frame, D. This latter is mounted on a vertical brass stage, E, which may be adjusted, radially and transversely, so as to facilitate the exact centring of the beam relative to the solenoid coils. These two coils are mounted in stirrups, V, anchored to the brass disk, F, which forms the upper portion of the instrument case, and may be rotated so as to bring varying amounts of the armatures within the solenoids. This movement allows the sensitivity of the galvanometer to be varied over a limited range, and also facilitates vertical adjustment of the solenoid positions when the instrument is initially assembled.

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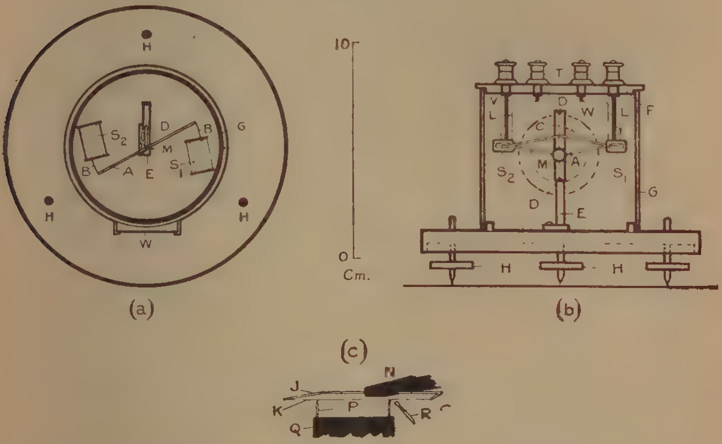
* Communicated by Prof. F. H. Newman, D.Sc., F.Inst.P.

Fig. 1.



(a) (b) (c)

The whole instrument is enclosed within a brass case, G, provided with a circular window, W, and mounted on a cast platform of brass, provided with three levelling screws, H.

The technique of mounting the suspension fibre follows the usual practice employed when dealing with quartz threads of very small diameter. A rectangular stirrup, P, fig. 1 (*c*), is first made by bending a length of quartz rod, 1 mm. diameter, in the pointed flame of a small hand blowpipe. The ends of the frame are then coated with fused shellac, and it is then mounted in a rectangular block of ebonite, Q, fig. 1 (*c*). The frame with its support is now placed in a suitable clamp, and the assembly is ready to receive the fibre. A selected quartz thread, K, fig. 1 (*c*), is now taken and stretched on the glass frame, J, fig. 1 (*c*), and its ends attached thereto, care being taken that the length of the fibre is slightly in excess over that required for the completed suspension. This glass frame is now carefully lowered by means of a clamp, N, fig. 1 (*c*), so that the fibre is just in contact with the ends of the quartz frame. While in this position, an additional tension is put on the fibre by slightly flexing the glass frame, and at the same time the shellac is melted with a fragment of heated glass rod, R, fig. 1 (*c*). When the shellac has thoroughly hardened, the excess fibre is carefully detached, leaving the complete suspension on its quartz support. This method of mounting ensures that the suspension shall be stretched as tightly as the tensile strength of the quartz thread will permit—a necessary condition for portability. Suspensions which give the slightest indication of "sagging" have been found to have a short useful life, as the excessive degree of lateral freedom given to the attached beam gives rise to shearing forces at the points of anchorage, and, in consequence, the fibre quickly breaks. The beam, A, fig. 1 (*a*) and (*b*), is attached to the fibre with two small globules, the complete suspension being arranged horizontally for this purpose, while the beam is carefully balanced on the fibre. When the equilibrium position is found the ends of the beam are supported so as to prevent possible movement, and the shellac beads are then fused to the fibre by applying a fragment of heated glass.

The leads, L, from the solenoid coils are joined to four insulated terminals, T, mounted on the disk, F, and this arrangement enables the coils to be joined "in series," or "in parallel," at will.

The period of the complete moving system is 5·5 sec.

Calibration of the Instrument.

The instrument has been calibrated, both with direct and alternating currents, by noting the deflexion produced by a measured current flowing in the solenoid coils, and separate calibration curves have been obtained for "series" and "parallel" coil connexions.

During the initial stages of the calibration considerable "hunting" of the zero was experienced, and in order to remedy this defect it was found necessary to screen the moving iron system from the effects of extraneous magnetic fields, by means of a tinplate cylinder fitted within the case of the instrument. As would be expected in a moving iron instrument, slight hysteresis effects were noticeable throughout the calibration, but there was no permanent zero displacement.

In calibrating the galvanometer it was joined in series with a variable 100,000 ohm standard resistance, a mercury key, and a Ferranti moving coil milliammeter (0–5 m.a.), incorporating a copper oxide rectifying unit for measuring the current in the alternating circuit. The output terminals of a "step-down" transformer ratio 110 : 12 furnished the potential required for the alternating current calibration, the current values being read directly from the milliammeter. Care was taken to insulate the solenoid coils, but, in spite of this precaution, some A.C. leakage took place through the medium of the instrument case, and this effect modified the character of the calibration curves obtained.

For the direct current calibration a 2 v. accumulator was used as the source of potential, the current values in this case being calculated from Ohm's law. Deflexions were measured by the lamp and scale method, the scale being 1 metre from the galvanometer mirror. The results obtained in calibrating the instrument both for direct and alternating currents are given in Tables I. and II.

The calibration curves, reproduced in figs. 2 and 3, were obtained by plotting values of current against deflexion in the calibration for direct current, and values of current against logarithm of deflexion for alternating current. The resulting curves are both linear.

Direct Current Calibration.

It has been found that with direct currents the deflexions of the galvanometer are directly porportional to the current passing through its coils, and for the coils connected "in series"

$$i = kd$$

where i=current in ampères, d=deflexion in millimetres (scale divisions), and K is a constant of the instrument having a value of $0{\cdot}82 \times 10^{-6}$. This gives a mean sensitivity of 0·82 microamps per mm. scale deflexion.

TABLE I.

Direct Current Calibration.

Series.			Parallel.		
Observed current $\times 10^{-5}$ amp.	Current value from curve $\times 10^{-5}$ amp.	Observed deflexion, mm.	Observed current $\times 10^{-5}$ amp.	Current value from curve $\times 10^{-5}$ amp.	Observed deflexion. mm.
1·96	1·87	24·0	1·99	1·93	12·5
2·17	2·12	26·0	2·21	2·16	14·0
2·43	2·36	29·0	2·48	2·39	15·5
2·77	2·72	33·5	2·84	2·86	18·5
3·22	3·17	39·0	3·30	3·24	21·0
3·88	3·82	47·0	3·96	3·94	25·5
4·75	4·75	58·5	4·94	4·94	32·0
6·23	6·29	77·5	6·55	6·57	42·5

TABLE II.

Alternating Current (50 cycles) Calibration.

Series.				Parallel.			
Observed current $\times 10^{-3}$ amp.	Current value from curve $\times 10^{-3}$ amp.	Observed deflexion D.	Log D.	Observed current $\times 10^{-3}$ amp.	Current value from curve $\times 10^{-3}$ amp.	Observed deflexion D.	Log D.
0·50	0·50	72·0	1·86	0·50	0·49	15·5	1·19
0·55	0·55	96·0	1·98	0·60	0·58	19·5	1·29
0·58	0·58	115·0	2·06	0·70	0·70	28·0	1·45
0·62	0·62	140·0	2·15	0·80	0·80	37·0	1·57
0·67	0·66	184·0	2·26	0·90	0·97	50·5	1·70
0·70	0·71	226·0	2·35	1·00	1·01	67·0	1·83
0·77	0·77	328·0	2·52	1·12	1·12	92·0	1·96
0·80	0·80	386·0	2·59	1·20	1·22	120·0	2·08

When the coils are connected "in parallel" the corresponding value for K is $1{\cdot}55 \times 10^{-6}$, and the sensitivity is 1·55 microamps per mm. scale deflexion. As would be expected, therefore, the sensitivity is approximately doubled by using the instrument with its coils joined "in series." It may be noted that theory indicates a parabolic relation existing between the values of current

Fig. 2.

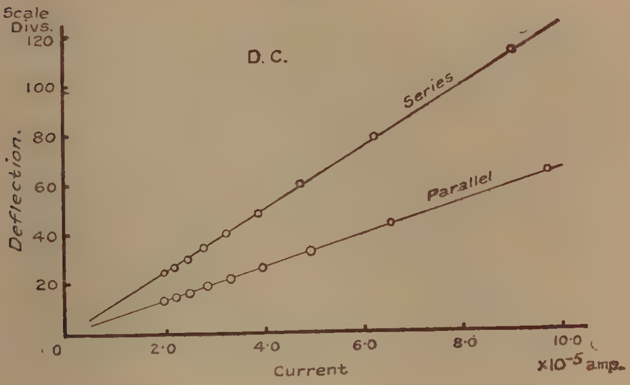
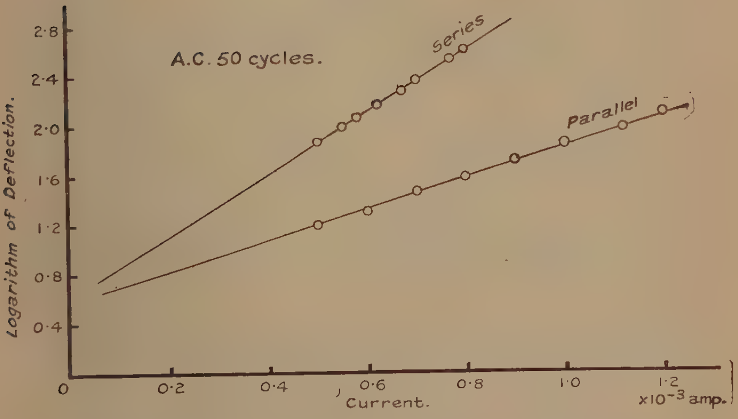


Fig. 3.



and corresponding deflexion, but this is not applicable to conditions existing during the actual calibration, since the theoretical consideration assumes a constant field value, whereas in practice the value of the permeability μ will vary continuously with the magnetizing current i.

Alternating Current Calibration.

The relation existing between the deflexion d and the virtual current i flowing in the solenoid coils may be represented by the equation

$$i=\beta\ (\log d-\alpha),$$

where β is the constant of the instrument, and α is the "zero-field" correction.

It will be seen from the curves connecting the values of i and $\log d$ that neither curve passes through the origin, and therefore there is a small residual deflexion α when the calibrating current value is zero. This effect may be explained by the presence of eddy currents induced in the solenoid coils, due to leakage through the case of the instrument. Since, however, the magnitude of this effect is practically constant throughout the entire current range, it may be allowed for in the corrected readings.

For values of β equal to $4{\cdot}0\times10^{-4}$ and $8{\cdot}1\times10^{-4}$ respectively for "series" and "parallel" calibration, the values of α are 0·61 and 0·58 respectively.

Summary.

1. A detailed description is given of a new type of galvanometer, employing a quartz fibre suspension, and suitable for use on direct or alternating current circuits.
2. Calibration curves for the instrument are given, and empirical formulæ are obtained giving the value of the current passing through the instrument in terms of the deflexion produced.

In conclusion, the author desires to thank Prof. F. H. Newman, D.Sc., for his kindly interest and helpful advice throughout this investigation.

CXIV. *The Capture of Electrons by Molecules.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the issue of your Magazine for last July there appears a communication by Prof. L. B. Loeb which is entirely devoted to attempting "to correct the erroneous impression given by Prof. Bailey's statements," and refers to a paper by Mr. J. D. McGee and myself which was published in the issue for December 1928. As Prof. Loeb appears to have an "erroneous impression" of our statements on pages 1088 and 1089, and himself makes some erroneous and inconsistent remarks, it seems desirable to comment briefly on his communication.

In a summary of the history of his own investigations he says: "It was shown that, using the *simplifying assumption* of a constant value of the constant of attachment n, a rigorous quantitative test of the theory should be possible by this means." On the next page he gives reasons why a quantitative study was *not possible*, and finds some other justification for regarding his results as being of value, namely, that his (and Wahlin's) estimates of n are correct in order of magnitude, and "still stand today as the only data even in order of magnitude bearing on this important electronic behaviour for any large range of substances." Anyone examining Prof. Loeb's work critically would naturally ask himself the following two questions:

(1) Has the "simplifying assumption" been established in any way?

(2) Would a serious error in the estimated value of n (or its order of magnitude) be likely if this assumption were incorrect?

As the work of Prof. Loeb and his associates (excepting Dr. Cravath) provides little definite information on these points, it is not unreasonable to regard their estimates with some reserve.

The information published in our paper on Ammonia enables us to go even further in our scepticism, for, apart from a large variation in the probability of attachment h $(=1/n)$ in the range 8 to 16 of the ratio X/p, we found our lowest estimate of h to be at least 1000 times larger than that found by Wahlin, which shows (as we stated) that either the "simplifying assumption" involved in Wahlin's estimate is enormously wrong, or else *our* sample of ammonia contained at least 1000 times more impurity than Wahlin's. We have not (as Prof. Loeb states) thrown any doubt on the purity of Wahlin's samples, nor have we said that Wahlin's estimate of 10^{-8} is wrong, since these matters need not be considered in order to conclude that "the results obtained with his (Loeb's) method, and set out in his table, may be quite misleading."

In referring to Cravath's work (by means of an original method), Prof. Loeb says: "Cravath has shown that, contrary to Bailey's belief, n in air also varies with the pressure . . . ."

It is difficult to regard this statement as an expression of Prof. Loeb's real views, for in the same paragraph he accepts my other conclusions, which could not have been reached without making the assumption that n depends *only* on the electronic energy (for a given gas); also it is unnecessary to go to Loeb's own writings to show that, until this latest one, he has held the same "belief"—it is attributed to him by Sir J. J. Thomson on page 13 of the same issue of the Philosophical Magazine. Finally Dr. Cravath himself expresses the following opinion * about the difference between the results of his experiments and mine: "..... the greater consistency of Bailey's data and the simpler conditions in his apparatus justify greater confidence in his results."

I may mention, in conclusion, that we hope soon to have ready for publication new experimental results which strengthen the arguments we have advanced.

Yours truly,
V. A. Bailey.

CXV. *Notices respecting New Books.*

Introduction à la Physique des Rayons X et Gamma. Par MM. Maurice et Louis de Broglie. (Paris: Gauthier Villars et Cie, 55 Quai des Grands-Augustins.)

Reference is made in the Preface of this book to some of the monographs which have appeared in recent years on the subject of X-rays and its many developments. This introduction to the study of X- and γ- rays gives a clear, concise, and up-to-date account of the nature of these rays, their scattering, with and without change of frequency, diffraction by crystals and the modification of Bragg's law, and, above all, the bearing of these discoveries on the structure of matter and radiation. The experiments of G. P. Thomson and others are described, confirming the hypothesis, brought forward some six years ago, of the wave character of a moving electron. In an appendix a brief account is given of the spinning electron of Uhlenbeck and Goudsmit and its application to the anomalous Zeeman effect and other problems.

Ions, Electrons, and Ionizing Radiations. By J. A. Crowther, Sc.D. Fifth edition. (Edward Arnold, Maddox Street, London, W. 1. Price 12*s*. 6*d*. net.)

The publication of the fifth edition of Prof. Crowther's well-known text-book is a sure indication that his work has roused the interest of many students of this branch of physical science and proved to be a useful introduction to the study of its recent developments. The author has submitted his book to a careful revision, and has added new sections describing some of the noteworthy researches carried out during the last few years—in particular, the latest work of Aston, Compton, G. P. Thomson, Millikan and Gerlach and Stern. New photographs of the tracks of ionizing radiations taken by Prof. C. T. R. Wilson replace those which appeared in earlier editions. References to original papers are given at the end of the chapters: a number of these contributions, especially those relating to X-rays and α-rays, have appeared in the pages of this Magazine.

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* A. M. Cravath, Phys. Rev., April 1929, p. 612.

Dynamics. By A. R. RAMSEY, M.A. (Cambridge University Press, Fetter Lane, London, E.C. 4. Price 10*s.* 6*d.* net.)

ALTHOUGH this book is claimed to be a text-book of elementary dynamics, it is intended to meet the requirements of pupils in upper forms who are preparing for Honours courses in applied mathematics. The author has drawn on his wide experience as a teacher of this subject, and has written a concise and useful text-book dealing with the ordinary syllabus in dynamics, with some sections of the subject not usually included in an introductory course. Among such may be mentioned motion in a resisting medium, to which the author refers in the Preface, and the problem of orbital motion as modified by the introduction of the small relativity term. Two chapters are devoted to harmonic motion and its applications and to the problem of small oscillations and the stability of motion. In addition to the exercises given at the end of each chapter, a large number of examples, elementary and advanced, are worked out for the guidance of the reader.

Standard Tables of Square Roots. By L. M. MILNE-THOMSON, M.A. (Geo. Bell & Sons, Ltd., York House, Portugal Street, London, W.C. 2. Price 7*s.* 6*d.* net.)

THE author has constructed a very useful and comprehensive table of square roots to eight places of decimals. Square roots of x and $10x$ are set out on the same page with first differences for four-figure values of the argument. Except in the earlier part of the table, linear interpolation is sufficient to give intermediate values of the square root to eight significant figures. A short table is given for the correction of first differences and the division method of computing square roots to fourteen places is explained and illustrated. The Standard Table will be a welcome addition to the equipment of those engaged in computing work, especially in the construction of tables of elliptic and other functions.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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